COAL-TAR AND AMMONIA

PART II—COAL-TAR

COAL-TAR AND AMMONIA

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PART II

COAL-TAR—*Continued*

CHAPTER XI

WORKING-UP THE LIGHT NAPHTHA INTO FINAL PRODUCTS

THE last rectification of light coal-tar oils is always effected by means of *steam*, either indirectly applied (dry steam) or blown directly into the liquid. In the latter case the steam carries away a large amount of substances boiling at a higher temperature than its own (according to the principles explained, p. 443); and it is hence reserved for the last stage, after the indirect steam has exhausted its action. As a rule, the steam-stills are adapted to both purposes. They also always possess some arrangement for partial condensation or dephlegmation, in order to effect a better separation of the final products.

The steam ought to have a tension of at least 2½ atmospheres, preferably more, but in any case as regular as possible. It should be, if not exactly superheated, at least completely dried—*e.g.*, by passing it through a coil of pipes, or through a long and shallow iron box, surrounded by the waste heat of the boiler-fire. The tension in the steam-boiler itself must, of course, be higher than the above, preferably at least 5 atmospheres.

The apparatus employed for this final distillation varies greatly. Smaller factories use stills with simple dephlegmators in the shape of worms or tubes. Larger works employ column-apparatus, which admit of obtaining the final products without repeated distillation of the intermediate fractions.

The final products of general trade, into which the total crude benzol should be split up without residues, are the following:—

	Furnishes distillate per cent. up to					Spec. grav.
	100°	120°	180°	160°	200°	
90 per cent. benzol .	90	...	...	...	...	0·885
50 per cent. benzol .	50	90	...	...	...	0·880
Solvent-naphtha .	...	...	20	90	...	0·875
Heavy naphtha .	...	...	...	...	90	0·880

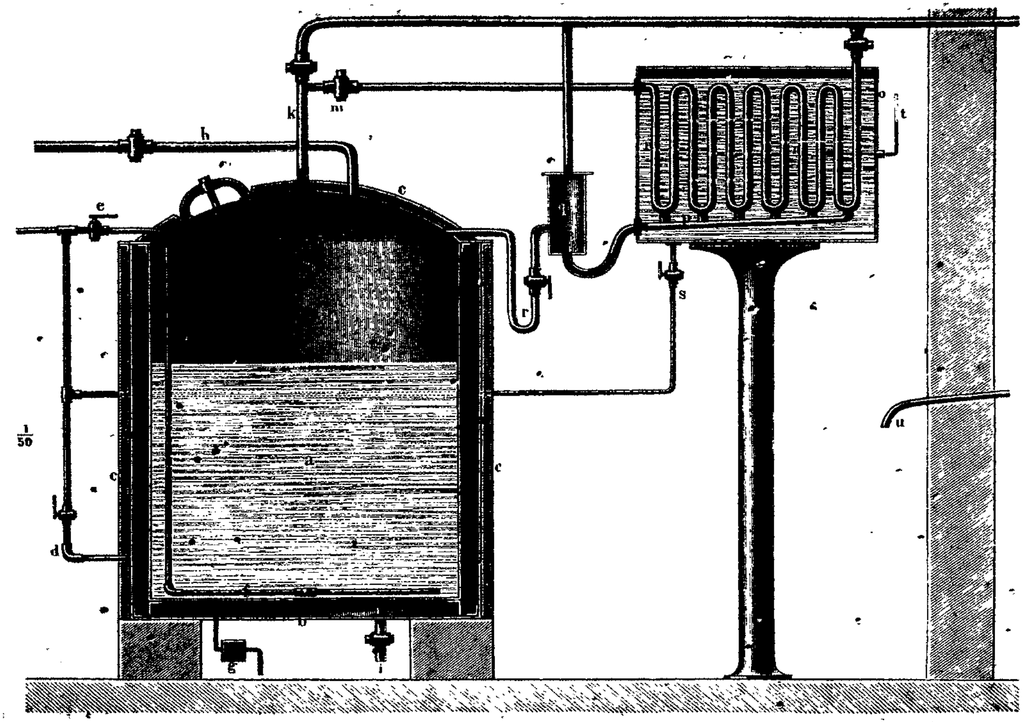
Since for the purpose of manufacturing artificial colours, for other synthetic and for various general purposes a large demand for the *pure* hydrocarbons has sprung up, these now also form one of the branches of many tar-distilleries; but many of these leave that final treatment to their customers and stop at the *commercial* products just mentioned, the manufacture of which we shall describe in the first instance.

English Steam-stills.

We shall first sketch two different systems of steam-stills, the principal parts of which may be mutually exchanged, so that the dephlegmator of the second system can be attached to the first still, and so on.

Fig. 188, p. 908, shows a system found in operation at large English tar-works. *a* is the still, made of boiler-plate, cylindrical, with flat bottom and convex top; *b b* is a wrought-iron jacket round the sides and bottom; *c*, a non-conducting casing of some sort for preventing the loss of heat; *d* and *e* are steam-cocks, *d* supplying the steam-jacket, *e* the perforated coil *f* inside the still; *g* is a self-acting water-injector for the coil *f*. The pipe *h* serves for feeding the still with crude benzol, *i* for discharging the residue, *k* for carrying away the vapours. The latter pipe communicates by the tap *l* directly with the worm, placed outside the still-house, or else, when *l* is shut and *m* is opened, first with the dephlegmator or "condenser" *n n*, made of lead or iron tubes. The latter is placed in the water-filled vessel *o*. The liquid condensing in *n n* collects in *p*, and flows through the vessel *q* and the hydraulic lute *r* back into the still. *q* sends a branch into the main vapour-pipe; but the bends of the pipes prevent the vapours from passing directly from *a* into *q* and thus into the worm. Through the steam-pipe *s* the water in *o* can be heated at will, this being regulated by the thermometer *t*. *u* is the bottom end of the worm, returning into the still-house.

In the second system (Fig. 189, p. 909, the similar or analogous parts are denoted by the same letters as in Fig. 188), *a* is the still, indirectly heated by steam entering through the steam-tap *d*, which communicates with a leaden or wrought-iron coil *b* with water-ejector *g*. Direct steam can be blown in-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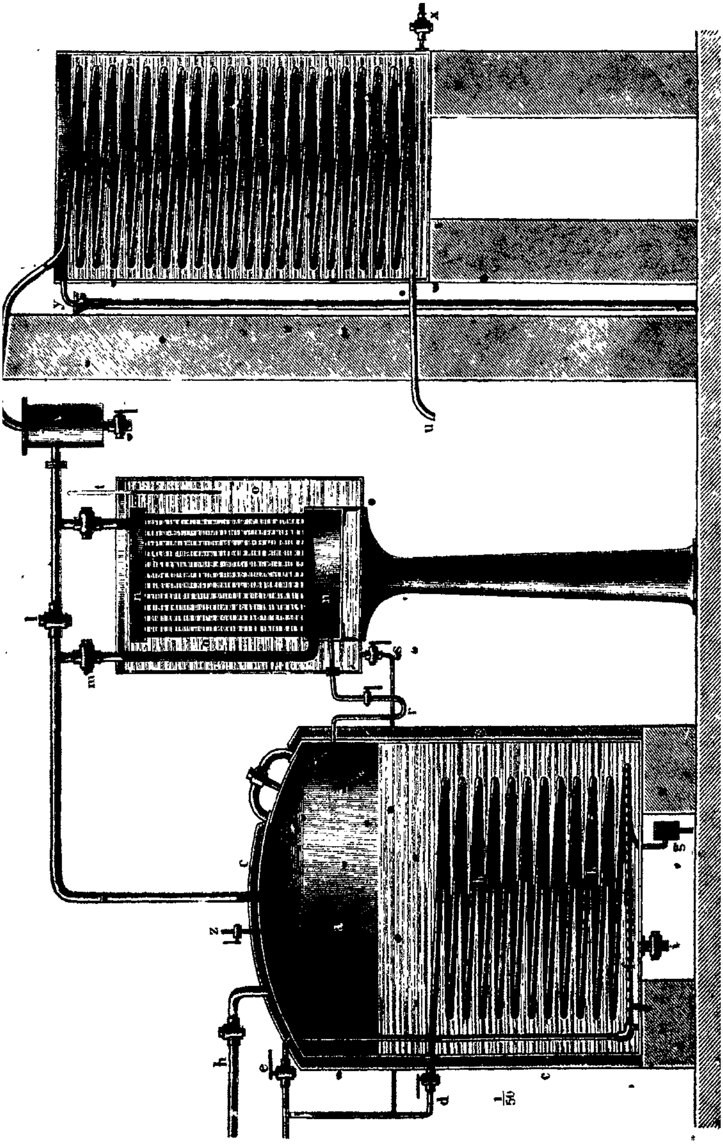
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through the tap *e* and the perforated cross of pipes *f*. *h* is the feed-pipe, *i* the delivery-cock, *k* the still-head. To carry the vapours away at once, the tap *l* is opened, when they first pass through the box *v* (for retaining any liquid carried over mechanically—a contrivance which should never be absent), and then enter the worm *w*, made of 1½-in. lead pipe, whose end at *u* returns into the still-house, where also the receivers are placed. The worm-tub is fed with water by *x*; at *y* the hot water runs off. If the vapours are to be dephlegmated, the tap *l* is closed and *m* opened. The vapours then enter the condenser *n n*, whose lower drum communicates with the upper one by fifty copper pipes of ⅜-in. bore. The condensed oil returns into the still by the hydraulic lute *r*; *s* is the steam-pipe for *o*, *t* the thermometer.

The second system appears to be superior to the first. Internal heating by a steam-coil is quicker and attended by less loss of heat than heating by a steam-jacket; and the dephlegmator represented in Fig. 189 especially acts more thoroughly, and impedes the passage of the vapours less than that shown in Fig. 188. Either is preferable to a simple worm, in which the ascending vapours are sometimes stopped by the backflow of condensing oils. Some manufacturers employ proper rectification-columns, as will be described later on in connection with Savalle's apparatus.

C. Lührig (Ger. P. 26679) employs a zigzag pipe, enclosed in another of a similar kind; the cooling-water runs in the annular space opposite the course of the vapours; at each downward bend of the pipe there is a branch pipe for taking away the condensed liquor.

C. A. Burghardt employs an inner cylinder, built up of tubes, *a* separated by perforated plates *b* (Fig. 190, p. 911), made of wire-gauze, which, being of greater diameter than the condenser, have their outer rims cooled by the water in the outer cylinder *c*. The vapours pass in at *d*, and are drawn through the apparatus by connecting the upper part at *e* with a draught. The condensed liquid flows by means of the tubes *f* and *g* into the receiver *h*. If this condenser is placed horizontally, the liquid condensing between the single plates *b b* can be drawn off in different states of purity (cf. *J. Soc. Chem. Ind.*, 1885, p. 475).

Another condenser has been patented by L. & C. Stein-müller (Ger. P. 31238); it consists of a series of tubes running parallel to each other in a horizontal direction, and cooled by a number of water-jets along their whole length.

Working the Stills.—The steam-stills are charged with washed naphtha either by means of a pump or an air-pressure apparatus, or else from a store-tank placed in an elevated position, into which the naphtha has first been pumped. Meanwhile the air-vent (seen at *c* in Fig. 189) is opened (it is either a tap or simply a 1-in. aperture), and afterwards closed by a cork or a screw-plug. Through this hole an iron gauge-rod can be introduced, in order to ascertain the level of the liquid in the still. The manhole is only opened at longer intervals, for cleaning the still.

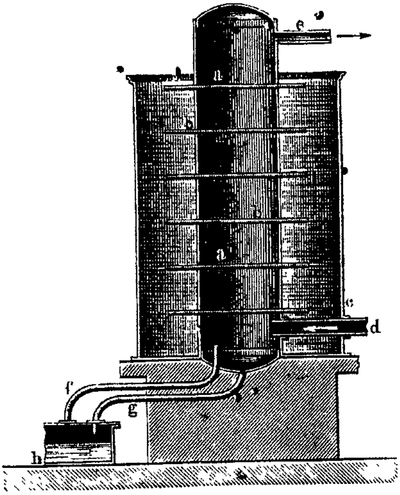

FIG. 190.

It is the rule to pump first the most volatile products into the still, and work them by indirect (dry) steam, and afterwards the less volatile products, which are first treated by indirect and afterwards by direct steam. If two products have been made in the benzol-still (p. 925), they are worked separately—viz., the second at once with direct steam, which can be done in a special still fitted merely with an arrangement for blowing in.

open steam; the distillation of the first product we shall now describe.

Steam is admitted with full force through the tap *d* into the steam-jacket or the steam-coil *b* (the letters refer both to Figs. 188 and 189). As soon as the liquid begins to boil and to distil, the steam-tap is almost closed, and is then regulated so that the distillation goes on continuously, but not too quickly, not to say tempestuously; otherwise there would be loss by incomplete condensation and also danger of fire. At first a little water comes over, which often makes the benzol quite turbid; but this need not be minded, as the benzol soon clears up, either in the receiver or in the store-tanks. Later on, when direct steam has to be used, of course very much water appears which must be separated from the naphtha. This can be done by the apparatus shown in Fig. 191, for instance, which at the same time permits the naphtha to be finally purified by dilute caustic-acid solution. Two open cylinders of tin-plate, *a* and *b*, 9 in. wide and 2 ft. high, are each provided at the top with a channel, serving as a water-lute, into which a tin cover is put; they are connected by the two pipes *c* and *d*, which can be quickly joined or separated by the screw-cap *e*; *c* ends open 1 in. below the top of *a*; *d* bends down inside *b*, and ends just above its bottom. From the bottom of *a* the pipe *f* rises up, passes out and leads to a waste-pipe; it can be shut off by *g*. From *b* the pipe *h* takes away any liquid just below the top. *g* and *e* must leave *a* exactly at the same level; *h* may be at the same or at a slightly lower level. At *i* the end of the cooling-worm is sketched.

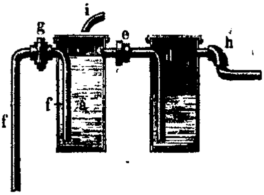

FIG. 191.

Before starting, *a* is three-quarters filled with water. As soon as the mixture of naphtha and water comes out of *i*, *a* is quickly filled up to the level of *c* and *f*, and its contents run out of these two pipes; but as water and naphtha instantly separate, only naphtha will run away from the top (through *c*), and only water from the bottom (through *f*). If *f* were below *c*, the former would fill entirely and act as a siphon, which should not take place. For use in case of need the tap *g* is provided; but this should never be required.

From *c*, the naphtha runs over into *b*, fills this vessel, and runs away into the receivers through *h*. At the last stage, *b* is half filled with dilute caustic-soda solution (sp. gr. 1·10), so that the naphtha must pass through it; why, we shall see later on.

At least *two receivers* are needed; these suffice, if the distillates are run or pumped straight from them into store-tanks; but some distillers prefer receiving the distillates in a large number of smaller drums, which facilitates the classing of the products. Instead of closed iron tanks, open vessels with loose covers are preferable as receivers, since these can be easily inspected and cleaned after every operation, so as to ensure that the final products are quite pure and colourless. In this case, since iron would rust quickly and the water would cause a red mud to be formed, wooden boxes lined with zinc or lead are employed, with their bottom sloping a little to one side, and a tap fixed at the lowest point, so as to draw off their contents completely, either into a store-tank or by means of a pump.

Koppers (Ger. P. 277189) regulates the supply of heat to the benzol-still by the quantity of the liquid run out of the heating-apparatus.

The usual process for separating the distillates is as follows:—First, as above mentioned, only indirect steam is admitted through the top *d* (Figs. 188 or 189). The most volatile products escape first; but from the first, along with benzene, a little toluene also distils, and later on much more, which is unavoidable in any fractional distillation, as explained, p. 443. But since in trade specific qualities of commercial "benzol" are required, means must be sought for obtaining these as directly as possible, with the least possible quantity of intermediate products to be worked over again. For this purpose the principle of *partially condensing the vapours*, with reflux of the condensate into the still, is always employed, as was done long ago by Mansfield; this is the same as has long been known in spirit-distilling as *dephlegmation*. It is effected by the condenser *n n*, in the vessel *o*. By closing the tap *l* and opening *m*, the vapours arriving by *k* are compelled to enter *n n*, the water in *o* being heated by the steam-pipe *s* to the required temperature. For 90 per cent. benzol the water-bath should be kept at 60°, for 50 per cent. benzol at 70° to 80°; but these temperatures cannot be absolutely fixed beforehand and must be found out by experience for each apparatus; in any case they should be kept as constant as possible. The liquor condensing in *n n* returns through *r* into the still *a*; it is essentially toluene, with a little benzene. Some manufacturers allow it to run back into *a* directly and continuously (Fig. 189); others interpose a small intermediate vessel (*q*, Fig. 188), if the shape of the condensers makes it more advisable to allow the vapours given off in *g* to get into the main delivery-pipe. Others run the condensate from *n* into a separate closed receiver, in order to rectify it separately. The uncondensed vapours of benzene, with a little toluene, now enter the main vapour-delivery pipe, then the worm *w*; and the benzol condensed therein runs through *u* and the separating-cans, Fig. 191, into the receivers.

After some time, nothing further will come out of *u*; and now the temperature in *o* should be raised to obtain weaker benzol. Usually it is possible, even for making pure toluene, to work with water in *o*, heating it to the boiling-point. Water is all the more applicable, if only 30 or 40 per cent. benzol is to be made at this stage, which is the rule. At most tar-works, in the further distillation no separation into pure hydrocarbons is aimed at, and hence the dephlegmation is not carried further. When nothing more runs from the worm *w*, the condenser *n* is put out of work by closing the tap *m* and opening *l*. Now all vapours pass directly into *w* and are condensed, so that again a considerable quantity of distillate is obtained. Gradually this ceases; and when little or nothing comes over, the indirect steam from *d* is stopped and direct steam is injected through *e* and the apertures of *f*. Even with steam of only 2½ or 3 atmospheres an ample quantity of xylene, trimethylbenzenes, and some tetramethylbenzenes is carried over, which mixture we shall subsequently describe as solvent- and burning-naphtha. Xylene is now employed as such in the manufacture of colours, and is for this purpose separated in Savalle's column-apparatus (see below).

We must now see on what principles the *fractionation* takes place. It seems the simplest course to be guided by the thermometer in the still or in the dephlegmator; but as the first requirement is to obtain products fulfilling certain commercial tests, and it is not very easy to carry this out by means of the thermometer alone, other matters must be taken into account. We shall first describe the process carried on at a tar-works possessing a still with rectifying-column, and working chiefly by the thermometer. Distillation by steam is there performed *twice*. In the first distillation the following fractions are made:—

1st, up to 103° (thermometer in the still), yields 65 to 70 per cent. benzol.
2nd, 103° to 110°, yields 30 per cent. benzol.
3rd, 110° to 130°, yields nothing at 100°, 60 per cent. at 120°.
4th, above 130°, yields solvent-naphtha.

In the second distillation the dephlegmator has the principal work to do. By rectifying fraction 1 and keeping the dephlegmator at 56°, 90 per cent. benzol is obtained; with the dephlegmator at 80°, 50 per cent. benzol comes out. The thermometer in the still, as long as 90 per cent. benzol comes, never exceeds 100°. When this temperature has been reached, fraction 2 of the first distillation is run in, and the temperature in the still is allowed to rise to 105°, that of the dephlegmator to 80°; the receiver is also changed, and 54 per cent. benzol obtained. Now the receiver is changed again, open steam is injected into the still, and the distillate collected as solvent-naphtha. It would be quite possible in the same apparatus to make pure toluene.

Other manufacturers are not guided by the temperature in the still, but only by that of the dephlegmator; and this seems preferable. It is certain that after some experiments with any special apparatus, and conducting the previous operations on the same plan, the regulation of the temperature of the dephlegmator will by itself permit any desired product to be obtained; *e.g.*, it will be possible to manage so that the whole distillate, when it is mixed up, shall yield 50 per cent. benzol. The receiver will then be charged for the first time when nothing further passes through the dephlegmator, for the second time when indirect steam does not yield anything even after shutting off the dephlegmator; so that a third product is to be obtained by open steam.

None of these marks can be implicitly trusted to furnish products fulfilling distinct commercial requirements. Hence during the operations several laboratory tests must be made; and some manufacturers depend entirely upon these. The testing is done in a glass retort, or, better, in a fractionating-flask with Liebig's condenser (Fig. 181, p. 868), taking as fixed points for the fractions only 100° and 120°, and for the later distillates also 130° and 160°.

Silbermann (Ger. P. 186876) describes an apparatus for the *self-acting control of fractional distillations.* The distillates run through a vessel in which a hydrometer is floating which, as its position is influenced by the varying density of the distillates, sets adjustable electricable contacts in motion. These serve on the one hand for opening the communication with the receivers intended to take the distillates of a certain density, and on the other hand for closing the communication with the receiver for the distillate of the next lower density; they also give an optical or acoustical sign in the laboratory or office. Special arrangements are provided for removing the hydrometer without interfering with the taps already closed.

Fractions obtained.—In most cases a previous laboratory test of the charge in the steam-still will give an approximate idea how much of every fraction may be expected. The description and tables given by Davis (*cf.* later on) are intended to indicate beforehand how much of the different products can be run from the still. In accordance with this, a sample is taken a short time before it is thought the receiver will have to be changed, after well mixing up its contents. Supposing 90 *per cent. benzol* to be aimed at, if the test shows that the contents of the receiver just give 90 per cent. at 100°, of course the receiver must be immediately changed, since it cannot be expected that this strength will remain for any length of time if the distillation be continued. Properly speaking, the distillate should always be rather stronger than necessary before being pumped into the store-tanks, to make quite sure of its being sufficiently strong for the purpose intended. Before being pumped away, its height in the receiver is gauged, and the volume (to be ascertained by a table) and analysis are noted. It must now be brought to exactly the proper strength by adding a calculated quantity of the contents of the next receiver. Supposing this to be found = 70 per cent. benzol, its contents will have to be divided among the store-tanks for 90 and 50 per cent. benzol. The calculation is made in the following manner:—Supposing 120 gall. of 95 per cent. benzol to have been pumped from the first receiver, and 160 gall. of 73 per cent. benzol to be found in the second, the question is, how much of the latter must we pump to the former in order to obtain a commercial product of 90 per cent.? We shall learn this from the proportion:—

$$
\begin{aligned}
120 \times 95 + x \times 75 &= (120 + x)90 \\
120(95 - 90) &= x(90 - 75) \\
x &= \frac{120 \times 5}{15} = 40.
\end{aligned}
$$

That is to say, to the 120 gall. of 95 per cent. another 40 gall. of 75 per cent. should be added, to obtain 120 + 40 gall. of 90 per cent. The remaining 120 gall. of 75 per cent. benzol are pumped into the store-tank for 50 per cent. benzol, and both quantity and quality noted. Suppose now that the third receiver is found to contain, say, 144 gall. of 40 per cent. benzol. We shall then put:—

$$
\begin{aligned}
120 \times 75 + 144 \times 40 &= (120 + 144)x \\
x &= \frac{14760}{264} = 55{\cdot}9.
\end{aligned}
$$

This means, if the whole contents of the third receiver be pumped to the 12 gall. of 750 per cent., the mixture will still be 56 per cent. benzol, and will bear an addition from the contents of the next receiver. But the examples already given will suffice to show how the calculation is made for this or any similar case. Frequently the benzol in the tanks is kept rather above the standard, and is only brought down just before it is sent out; but care should be taken to do this invariably with the immediately following, not with any later fraction.

If no 90 per cent. benzol at all is required, all the above-mentioned distillates would be pumped into the tank for 50 per cent. benzol, always noting both quantity and quality. By multiplying each time the number of gallons by the percentage, and dividing the product by the total number of gallons, the percentage of the mixture will be found. The "percentage" in this case is no doubt only an apparent one; a 50 per cent. benzol has no analogy with a 50 per cent. solution of a salt or with 50 per cent. spirit-of-wine; but practice has shown that calculations like those exemplified are quite trustworthy. As a rule they make the product appear slightly below its actual strength; but this is a fault of which the buyer will not complain, and which the tar-distiller might easily correct if he cared to do so. In the case of important contracts, of course, such calculations will not be depended upon, but the mixture must be specially tested.

Hohenhausen (*J. Soc. Chem. Ind.*, 1884, p. 174) gives the following examples:—500 gall. of crude Yorkshire naphtha which before separation tested

At 110°	120°	130°
16	34	47 per cent.

yielded, as the first portion, with dry steam 250 gall. 40 per cent. benzol, testing

At 95°	100°	110°	120°
15	39	75	89 per cent.

Wigan crude naphtha, treated in the same way, yielded:

Sample A.	At 110°	120°	130°	140°	150°
500 gallons crude .	17	38	49	58	69 per cent.
	At 95°	100°	110°	120°	
200 gallons obtained by dry steam .	14	38	73	89 per cent.	
Sample B.	At 110°	120°	130°	140°	150°
500 gallons crude .	13	34	47	57	68 per cent.
	At 95°	100°	110°	120°	
200 gallons obtained by dry steam .	15	40	74	90 per cent.	

Besides 90 and 50 per cent. benzol, frequently 40 or even 30 per cent. benzol is required in trade. What now comes is mostly toluene, and is sometimes sold as such. Commercial *toluol* ought to yield 90 per cent. at 120°. But the next fraction after benzol is sometimes destined for *carburetting-naphtha.* According to a specification proposed by Dr Letheby and adopted by several gas-works, such naphtha ought to yield at least 70 per cent. at 130° and 90 per cent. at 150°; its sp. gr. ought to be 0·85 to 0·87. In practice, only the first point need be taken care of; the others will follow of course. This product essentially consists of *xylene*. The specific gravity proves the absence of any adulteration with petroleum spirit. When passing from benzol to carburetting-naphtha, half-filling the second separating-can (*b*, Fig. 191, p. 912) with weak caustic-soda solution should not be omitted. If there is no sale for this product, it is redistilled and split up into benzol and solvent-naphtha.

According to a table given in Wurtz's *Dictionnaire de Chimie*, i., p. 1663, French distillers would seem to fractionate in a different manner. The first principal fraction received consists of the tar-oils boiling from 30° to 150°. They are first redistilled in boilers of 2000 litres capacity by open fire or steam; two-thirds are distilled off, and the residual third run to the second fraction, viz., the oil boiling between 150° and 200°. The above two-thirds are treated with acid and alkali, and rectified afterwards, the following fractions being made:—

a. Boiling from 30° to 70°, pentane, hexane, etc.
b. „ „ 70° to 100°, benzene and toluene.
c. „ „ 110° to 127°, "solvent-naphtha" No. I. for removing grease.
d. „ „ 127° to 140°, "solvent-naphtha" No. II. for removing grease.
e. Residue, goes to the second principal fraction.

But it is not possible to separate the hydrocarbons so easily and completely as indicated by Wurtz. None of the tar-works known to the author proceed in this way.

Lipszyc (Fr. P. 473309) *deodorizes* benzol by treatment with an oxidizing agent, such as potassium or calcium permanganate in neutral or sulphuric acid solution, and subsequently washing with water and caustic soda. It is rendered *non-explosive* and *non-inflammable* by mixing it with 10 to 25 per cent. of trichloroethylene or with other chloro-hydrocarbons.

Solvent-Naphtha.—The distillate which follows the weakest benzol, or the toluol, is received as *solvent-naphtha;* and some manufacturers make no further fraction, but add to this also everything obtainable from the liquid by direct steam. The name is derived from the fact that this product is used for dissolving indiarubber in the manufacture of waterproof fabrics. It is extensively employed in the manufacture of anthracene (p. 609), in "chemical washing" for removing grease-spots, in the manufacture of varnishes and linoleum, in the extraction of the scent from flowers, etc., etc. It consists principally of xylenes and trimethylbenzenes, no doubt also of other bodies not well understood. The indiarubber manufacturers require the solvent-naphtha to be entirely free from naphthalene, which may occur in small quantity in the last distillate by steam. Hence the distillation should not be carried too far, but should be interrupted when the product yields 90 per cent. at 150° (some allow 160°), and its specific gravity does not exceed 0·875 at 15°. This will be the case with the whole as soon as a sample of the distillate, as it flows from the worm, shows 0·880 at 15°. Since differences in temperature cause very important differences in the specific gravity, it should never be neglected to reduce the observed to the normal temperature (which can be done by means of the table in the Appendix).

There are two qualities of solvent-naphtha found in the trade. Solvent-naphtha, No. I, on distillation, ought to yield 90 per cent. up to 160°, No. II 90 per cent. up to 175°. Both qualities ought to be free from bases and phenols, and well washed by sulphuric acid.

O. Jacobsen (*Annalen*, clxxxiv., p. 199) found in tar-oil distilling between 140° to 180°, corresponding to No. II of the solvent-naphtha now found in trade, pseudocumene, mesitylene, and an aliphatic hydrocarbon, decane.

Allen states that solvent-naphtha consists mainly of toluol and xylols, with sensible quantities of cumol and even higher homologues, together with a few per cent. of naphthalene. This is, however, not correct. There is very little toluol in solvent-naphtha, but, on the other hand, a good deal of trimethylbenzenes, and probably also of the tetramethylbenzenes found by K. E. Schulze (*vide supra*, p. 740); and there should be next to no naphthalene present. According to Weger the three trimethylbenzenes are present in solvent-naphtha in considerable quantities. Of these, the pseudocumene (1-2-4 trimethylbenzene) is prevalent, and is most easily obtained in the pure state, owing to the slight solubility of its sulphonic acid in sulphuric acid; the other two isomers, viz., mesitylene and hemellithol, are difficult to recover. Of the tetramethylbenzenes, durol is present, but the proper cumol (isopropylbenzene) seems to be absent. The greatest portion of the hydrocarbons boiling within the limits of solvent-naphtha has not yet been isolated.

Colman (*J. Gas Lighting*, 1915, cxxix., p. 314) gives special prescriptions for determining the percentage of toluene in commercial solvent-naphtha.

G. Schultz (*Berl. Ber.*, 1909, pp. 3602, 3609, 3613, 3617) has made (with several co-operators) a very extensive investigation of solvent-naphtha. He describes in detail the isolation of pseudocumene in the pure state, of normal decane, of *n*-propylbenzene, and of three isomeric ethyl-toluenes.

Solvent-naphtha, apart from its use as a solvent for indiarubber, is extensively employed for the purification of anthracene (*vide supra*, p. 609), in "chemical washing" for the removal of grease-spots, in the manufacture of common varnishes, in that of linoleum, for the extraction of scent from flowers, etc. Plehn (Ger. P. 156988) recommends adding from 5 to 30 per cent. of it to spirit of wine intended to serve as an illuminant. G. Schultz (B. P. 19565, of 1907) uses it in the manufacture of explosives.

Solvent-naphtha ought to have no very strong and disagreeable *smell;* this is not indicated by the sulphuric-acid reaction, as pointed out by Weger (*Z. angew. Chem.*, 1909, p. 341).

Burning-naphtha.—If special stipulations are made for the delivery of solvent-naphtha, and if, on the other hand, there is a sale for *heavy* or *burning-naphtha*, the last distillate is received as such. The operation is carried on up to the point at which the distillate begins to show a little colour. Then the steam is stopped at once, and the operation is finished. If the washing has been well done, the distillate remains colourless, and the end of the distillation must be judged of by other tests. Smell is a very distinct and characteristic test, but necessarily subjective; naphthalene especially will thus be detected. Another criterion (in this case a certain one) is the specific gravity, which should be 0·900 for the last sample running out of the worm, or 0·880 to 0·887 for the whole of the naphtha. A further test is made by shaking up the naphtha; only opalescent beads, instantly vanishing, ought to be formed, and no remaining froth. Moreover, it should not be discoloured when exposed to the sunlight for several days; it will then keep colourless in the dark for a long time.

The distillation of the 5 to 8 per cent. burning-naphtha which can be got from the distillate up to 140° C. of the benzol-still takes a comparatively very long time. Hence it is often preferred not to distil it at all up to this point, but to mix the residue remaining after getting out the solvent-naphtha with the fraction from the benzol-still boiling from 140° to 170°, which is distilled at once by open steam, and yields merely solvent- and burning-naphtha.

In all distillations by open steam the box for catching any liquid carried over (*v*, in Fig. 188) is essential for protecting the distillate from discoloration; it should be emptied at least once every day; the caustic liquor in *b*, Fig. 189, must also be renewed daily.

From the product distilling up to 140° may be expected 60 or 76 per cent. of 50 per cent. benzol, 20 or 25 per cent. of carburetting- and solvent-naphtha, 5 to 8 per cent. of burning-naphtha. The product distilling between 140° and 170° yields 25 to 50 per cent. best naphtha, 25 to 50 per cent. burning-naphtha, and 25 per cent. residue in the still, which it is best to pass through the light-oil still, although it generally sinks in water.

Apparatus for a Complete Separation of the Naphtha into Pure Benzene, Toluene, Xylene, etc.

Formerly most tar-distillers made only 90 or 50 per cent., sometimes 40 or 30 per cent. benzol, solvent- and burning-naphtha. Only exceptionally, and that mostly at the colour-works, a complete separation into benzene, toluene, xylene, etc., was aimed at; but during recent years this has been more and more the case, and in Germany it is practically the only process carried out at the larger tar-works. This complete separation can be effected by more perfect apparatus than those hitherto described, carrying out the principle of dephlegmation as completely, as this has long been done in the rectification of spirit of wine. Mansfield proposed this already in 1847; but it seems that Coupier, in 1863, first carried it out for the purpose of isolating each of the hydrocarbons in a nearly pure state

(*Bull. Soc. Ind. Mulhouse*, 1866, p. 260). His apparatus is shown in Fig. 192, on a scale on 1 : 50. A designates the lower

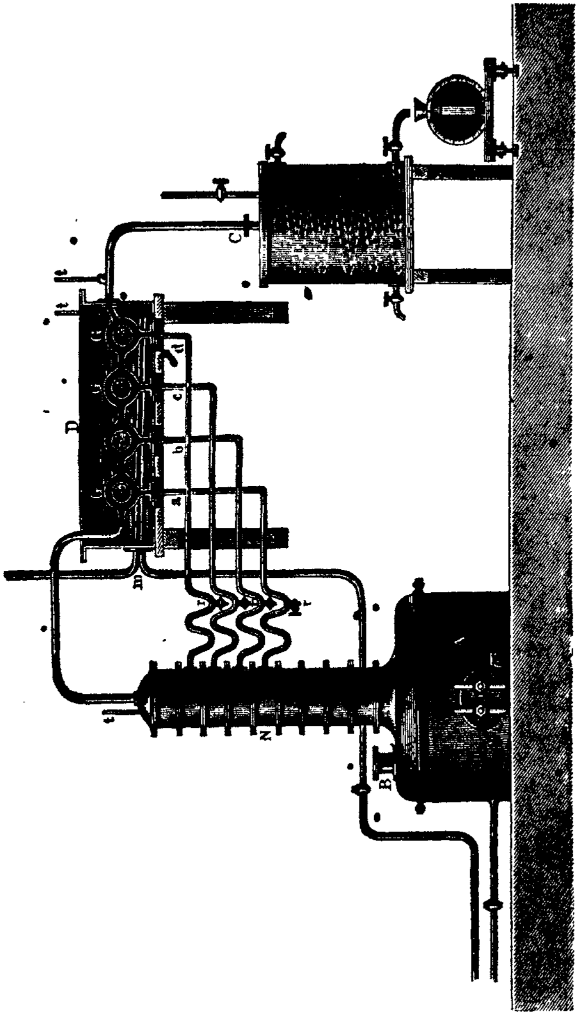

FIG. 192.

reservoir (the still proper), to which is attached a steam-pipe (forming a coil inside), a manhole, a discharge-cock, etc. B is the opening for feeding with crude benzol. The still is surmounted by the cast-iron rectification-column N, which will be described in detail below. The thermometer *t* is required for regulating the process. The heat of the steam-coil in A (the steam should be at a pressure of 2 atmospheres, or even more for the highest homologues) causes the liquid to boil. In the column N the least volatile oils are condensed by the cooling action of the air and run back into A. The more volatile vapours pass into the trough D, where they are kept at such a temperature that the hydrocarbons of lowest boiling-point remain in a state of vapour, whilst all the higher-boiling ones condense and flow back into the still. For this purpose the vapours pass through the annular spaces of the condensers, placed alongside one another, whose walls are washed inside and outside by the liquid contained in D. If only benzene and toluene are to be separated in the pure state, the liquid in D may be water; for the temperature in D should be kept (by means of the steam-coil *m* and the thermometer *t*) at 60° to 70° for benzene (boiling-point 80°·5) and at 100° for toluene (boiling-point 111°). If xylene or trimethylbenzenes are required, D would have to be filled with a solution of ammonium nitrate (boiling at 164°) or with paraffin.[1] What condenses in the annular condenser G G runs back to N, through the pipes *a*, *b*, *c*, *d*, whose bends prevent the passage of vapours from N to G G. It will be seen that the liquid first condensed enters the column at a lower place than that condensed afterwards. The taps *r r* serve for taking samples and testing the operation. The vapours issuing from the last condenser pass into the worm C, where they are completely condensed. If crude benzol is distilled, the water in D is first kept at 60° or 70°. When no more benzene comes out of C, the receiver is changed, and the temperature in D raised to 100°. At first a little of a mixture comes over; but soon pure toluene appears, which requires steam of 3½ atmospheres in A. When this ceases, the operation is usually stopped; but in case of need, xylenes and trimethylbenzenes can be isolated in a similar manner. Coupier has shown by the graphical diagram (Fig. 193) the quantity of principal and intermediate products obtained by his apparatus from 100 litres of crude benzol, boiling from 62° to 150° (say ordinary commercial 50 per cent. benzol).

---

[1] This would require steam of 6 to 7 atmospheres for the steam-coil in A; it is hardly ever done.

Hence 44 litres pure benzene and 17 pure toluene are obtained, and also:—(*a*) 6 litres first runnings, consisting partly of carbon disulphide, amylene, etc., which may be utilized by adding it to the solvent naphtha; (*b*) 6 litres of an intermediate product between benzene and toluene, which is redistilled; (*c*) about 27 litres high-boiling products, which formerly went at once into the solvent naphtha, but from which now the xylene (9 litres) is sometimes separated.

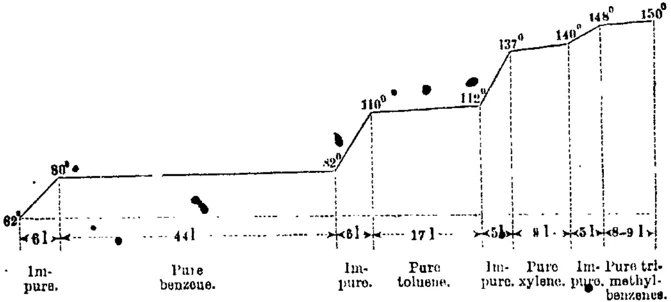

FIG. 193.

Figs. 194 and 195 show the plan and section of the com-

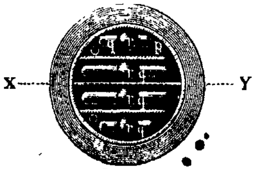

FIG. 194.

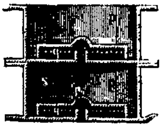

FIG. 195.

partments of the rectifying-column N (Fig. 192, p. 923) on a scale of 1 : 25. The vapours rise in the pipes *q*, but are checked by caps *r*, and must find their way through the apertures and the liquid standing over them. That liquid, consisting of the portion of the vapours condensed by the cooling action of the air, gradually flows through the overflow-tubes *s* from one plate into another. The labyrinth-partitions ("chicanes") *p p* cause the gas to remain in prolonged contact with the liquid, so as to precipitate the less volatile oils from the vapours, and to carry away by the heat of the latter the most volatile constituents of the liquid. The frequent repetition of this process in the nine or ten compartments of the column causes the fractionation to be much more thorough than even repeated rectifications without them would have made it.

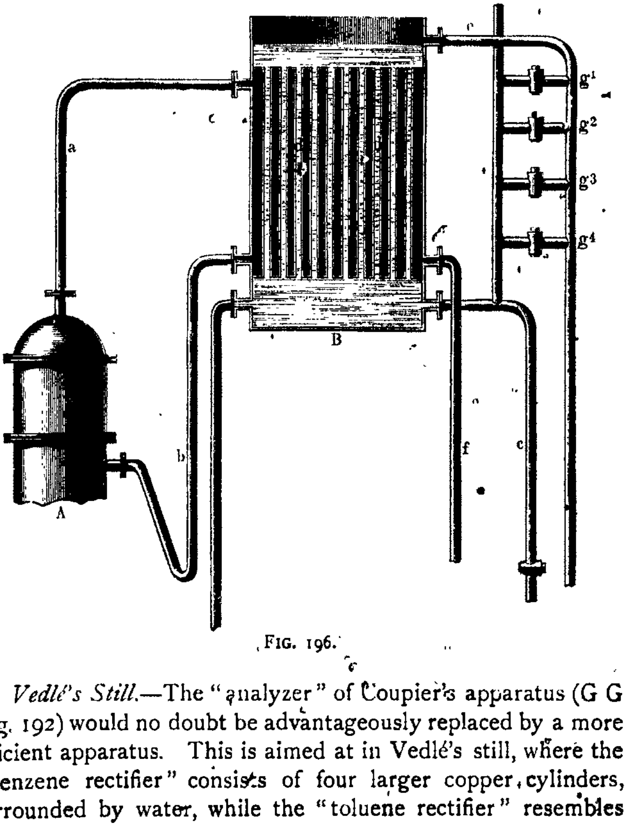

FIG. 196.

Vedlé's Still.—The "analyzer" of Coupier's apparatus (G G Fig. 192) would no doubt be advantageously replaced by a more efficient apparatus. This is aimed at in Vedlé's still, where the "benzene rectifier" consists of four larger copper cylinders, surrounded by water, while the "toluene rectifier" resembles that shown in our Fig. 184 (p. 875) at *n o*, and will be best understood from Fig. 196. The vapours pass from the still-head (rectifying-column) A into the analyzer B (6 ft. × 2 ft.) by the pipe *a*, and the condensed liquid back into A by the pipe *b*, while the uncondensed vapours pass away through *f* into an ordinary worm or condenser of any other form. The vessel B is separated into three parts by two partitions, connected by 60 copper tubes, *d d*, 1¼ in. wide. Water flows through *c* into the lower part of B, thence through *d d* into the upper part and away through *e*. When very little condensate is running out through *f*, the supply of water through *c* is stopped, and the contents of B are allowed to reach the boiling-point by the heat of the vapours coming from A. At this stage mostly toluene passes over. When this also ceases to flow, the level of water in B is lowered by successively opening the taps g^1 g^2 g^3 g^4, so that eventually the space in B is altogether filled with steam inside and with vapours of hydrocarbons outside the tubes *d d*. At this stage almost pure xylene passes over.

Egrot's apparatus (mentioned by Hohenhausen, in *J. Soc. Chem. Ind.*, 1884, p. 76) is not essentially different from Coupier's.

The rectifying apparatus of D. Savalle, fils, of Paris, enjoy special reputation for applicability to the hydrocarbons of coal-tar, and are largely employed by German tar-distillers even for 90 or 50 per cent. benzol. Figs. 197 to 200 represent this apparatus. In Fig. 197, A is the still, heated by a steam-coil; B, a square column for the first condensation; C, the air-condenser for the second condensation of the higher-boiling hydrocarbons which are not passed over into the distillate; D, the air-cooler, in which the distillate itself is condensed. The air is supplied by the fan-blast F, through H to C, and through I to D. J is the slide which regulates the current of air in the condenser, by means of a chain and a graduated lever, K. The liquid condensing in D passes through the check-apparatus G, for controlling the speed of the distillation. E is a regulator for maintaining a constant pressure in the apparatus throughout the distillation, L is the steam-engine supplying the fan-blast; 1, steam-valve of the regulator; 2, condensed-water ejector; 3, backflow-tap of the column; 4, purifying-tap of the same; 5, discharge-cock of the upper part of the column; 6, thermometer; 7, tap for discharging and charging the still.

The inner arrangement of the column is shown in Fig. 198. The vapours enter it by the cylinder *a*, divided by a vertical partition into compartments, and provided with a thermometer, *b*. The column is divided into several chambers by horizontal

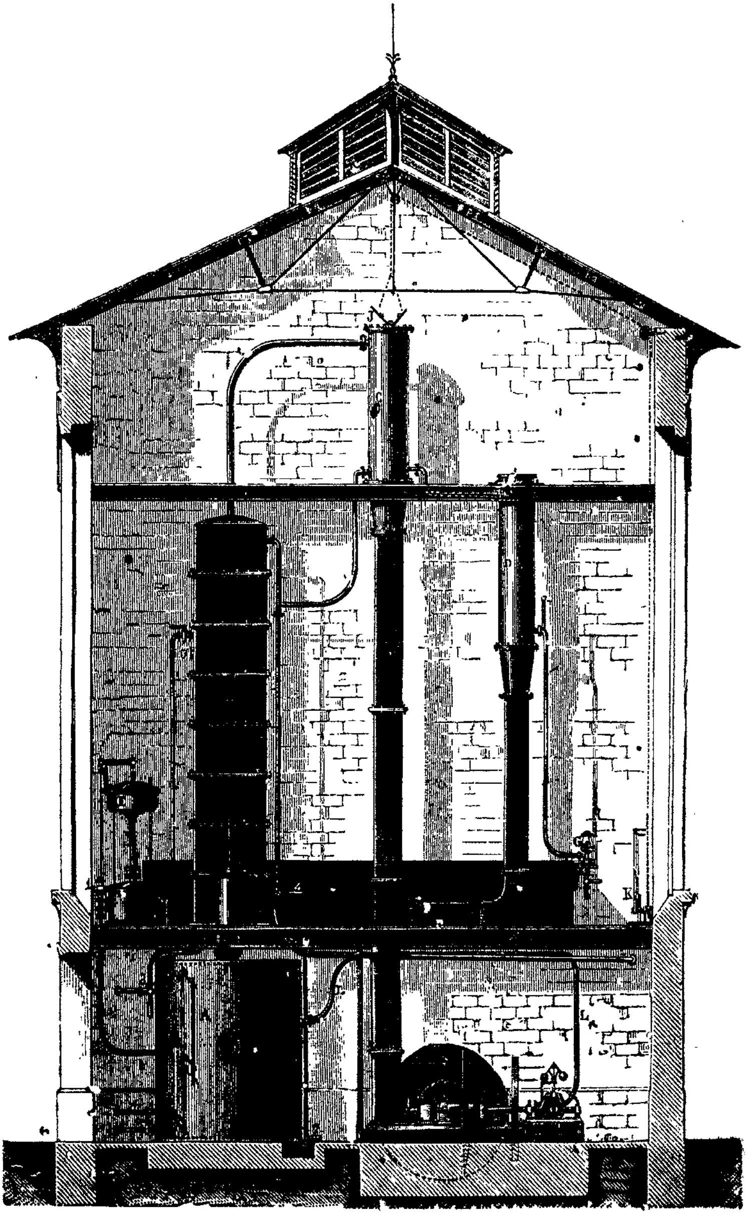

FIG. 107.

perforated partitions. Every partition contains a perpendicular overflow-pipe which partially dips into a corresponding recess of the next lower plate; these overflow-pipes are placed alternately on opposite sides. The higher-boiling products, flowing down the condenser, thus successively pass through all the chambers and finally go back into the column. The perforations of the plates are made of such diameter that the rising current of vapours prevents the liquid from falling through them, and a depth of about 2 in. of liquid (corresponding to the top of the overflow-pipes) always remains on the partitions: thus the vapours must always pass through the liquid, which considerably promotes the condensation of the higher-boiling products.

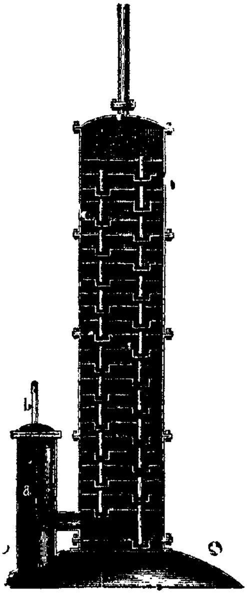

FIG. 198.

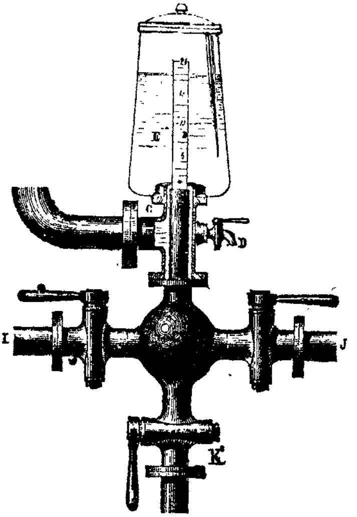

FIG. 199.

Fig. 199 shows the check-apparatus. The distillate from the cooler passes first into the annular space between the pipes C and F. The upper, graduated portion of the latter projects into the glass jar E, and has a small orifice at F. The space between C and F communicates with E. If the flow of the distillate is such that, with the pressure existing in the apparatus, it can run away through the orifice F, the liquid will not rise above this; but if the speed of flow is in excess of that, the liquid will rise from the annular space between C and F into the jar E. This will cause a hydraulic pressure, in consequence of which the distillate will pass more quickly through F. Thus a state of equilibrium will be produced; and it will be seen that the level of the liquid in the jar E, which can be read off on the

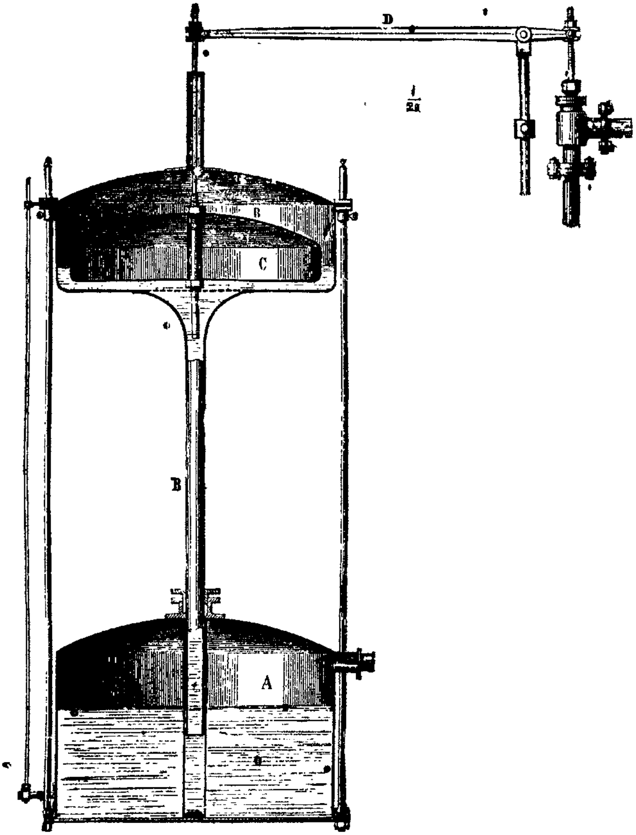

FIG. 200.

graduation of F, depends upon the speed of flow of the distillate. Hence, on the other hand, the latter may be inferred from the former. The size of the orifice in F must of course be regulated once for all on starting the apparatus. The graduation on F is arranged so as to show the quantity of liquid passing hourly through the apparatus; and a glance at it suffices to show whether the proper quantity of distillate per hour is delivered—that is, whether the apparatus is in order or not. D is a tap for taking samples.

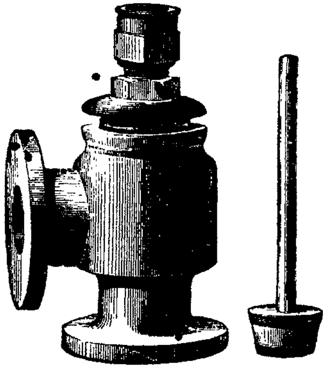

FIG. 201.

Fig. 200 shows the arrangement of the pressure-regulator. It consists of two superposed vessels connected by a pipe, B. The lower vessel, A, is partly filled with water, and communicates through F (Fig. 199) with the rectifying-column. The upper vessel is provided with a float, C, acting by the lever D upon the conical valve in E. The latter communicates both with the steam-boiler and with the steam-coil heating the still. As soon as pressure is produced in the apparatus, the water must rise in the pipe B, and when the pressure has attained a certain degree, the water will enter the upper vessel and lift the float C. This depresses the valve E and checks the supply of steam. If by some accident, such as choking up, the pressure in the still should rise too high, the regulator will shut off the steam entirely. By suitable adjustment it can be managed so that, in consequence of the action of the regulator, a certain pressure is never exceeded, which is important both for obtaining a constant product and for preventing accidents.

Fig. 201 shows the steam-valve, moved by the regulator. Further details on Savalle's apparatus for rectifying spirit

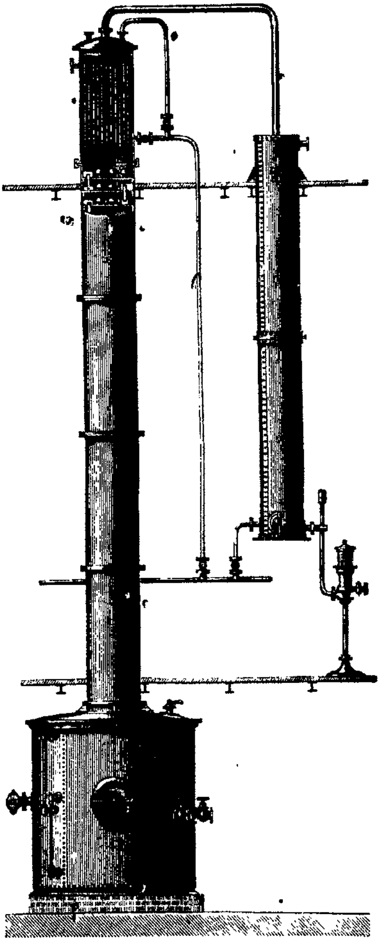

FIG. 202.

will be found in the Bulletin de la Société d'Encouragement, 1876, p. 657 (*Dingl. polyt. J.*, ccxxiii., p. 615), and in a pamphlet by Désiré Savalle, "Appareils et Procédés nouveaux de Distillation" (Paris, G. Masson, 1876, 223 pages and 48 diagrams).

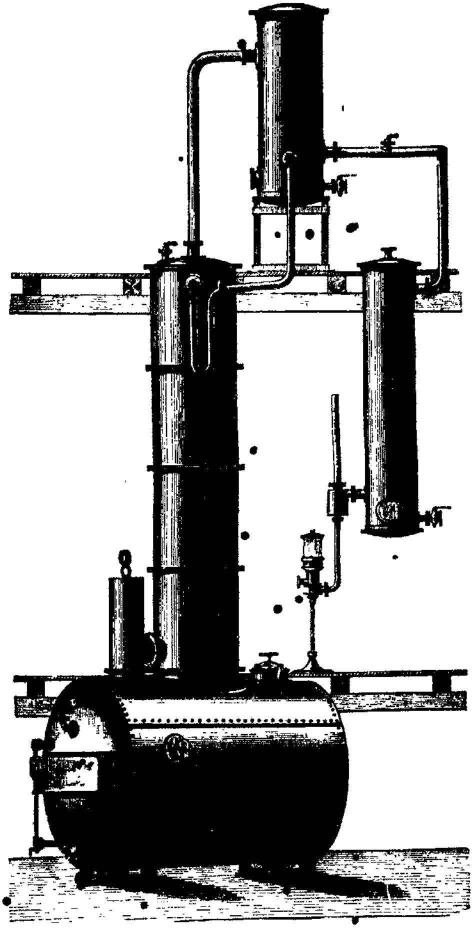

FIG. 203.

The original Savalle apparatus was made of copper; but for benzol cast-iron apparatus are frequently employed, and some manufacturers have such apparatus on a similar principle to, but not identical with Savalle's. The air-cooling system originally employed by Savalle for the rectification of spirit of wine has been everywhere replaced by water-cooling, as it was not efficient.

Figs. 202 and 203 show the Savalle column as improved by Heckmann (Ger. P., 39557) by the introduction of bell lutes, intended to avoid any drops of liquid being carried upwards with the steam. The plates of this column are not perforated, and are attached to the sides of the column, far apart. They are supposed to effect a saving of 40 per cent. against other columns. The dephlegmators and condensers are so arranged that the steam is cooled quite evenly right through. This apparatus is made either of copper or of iron. For benzol, iron is usually employed, inclusive of taps and valves; riveting and soldering is almost entirely avoided; the heating-worms can be taken out in one piece, and all repairs can be effected without the men having to get inside the still.

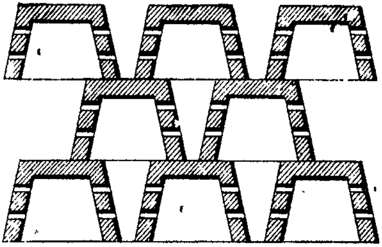

FIG. 204.

Instead of the various intermediate horizontal partitions, shown in the above-described apparatus, the column may be filled with conical pots with perforated or fluted sides, placed over one another, as shown in Fig. 204, so as to break up the current of vapours into many small currents, which suffer innumerable shocks against solid surfaces.

J. H. Miller (B. P. 25469, 1901) describes an apparatus for fractional distillation, containing no rectifying diaphragms, but consisting only of one tube, several metres long, with an inner concentric tube, provided with a great number of holes. There may be two or more columns of this kind combined.

By such columns it is possible to obtain from chemically washed first runnings in one operation commercial 90 per cent. benzol, 50 per cent. benzol, and solvent-naphtha. When starting with 50 per cent. benzol, according to Häussermann (*Z. angew. Chem.*, 1892, p. 131), pure benzene can be obtained, boiling within 0°·5 and completely solidifying in the cold.

Werner and Pfleiderer (Ger. P. 106713) have constructed an apparatus for continuous, automatic fractionation and partial rectification.

Another apparatus for the continuous separation of benzene, toluene, and xylene (also for similar purposes in the rectification of petroleum) is described in the German patent, No. 194567, of Kubierschky, which is discussed in detail by Borrmann (*Chem. Zeit.*, 1909, pp. 426 and 737; 1911, No. 39).

The *diameter of the fractionating-columns* for benzol must, of course, vary with the size of the still. According to Spilker (*loc. cit.*, p. 60) it should be about 2 ft. 8 in. for stills holding 5000 litres (= 176·6 cub. ft.) and 3 ft. 3 in. for 10,000 litres (= 353 cub. ft.). Their efficiency increases with their size, especially if the number of the plates is correspondingly increased.

Coolers.—The proportion and efficiency of the coolers must, of course, be greater for benzol stills than for the distillation of the tar or of the crude oils, because the danger of losses caused by incomplete cooling is much greater. The cooling-surface must be greater, and counter-current coolers should be employed, which are more efficient than serpentine or tubular coolers, while occupying less space. Such a cooler is supplied by the Berlin-Anhaltische Maschinenbau-Aktiengesellschaft, according to Uhlmann's patent. That cooler is composed of a number of cells, made of cast-iron, lead, or other suitable metal, in which the space traversed by the cooling-agent is provided by two plates, inclining from the side where the cooling-agent enters towards the other side of the cell, and divided by a partition not going quite up to the opposite side. This arrangement produces a very large cooling-surface in a small space, all the more as it provides for two separate currents of the cooling-agent passing through. The water- and gas-spaces are accessible for cleaning by taking off caps from the necks, without dismounting the apparatus. Such a cooler, with a cooling-surface of 32 superficial feet, weighs about 26 cwt. in the empty state, and about 30 cwt. when filled with water; whereas a cast-iron worm-cooler doing the same duty must possess about 160 superficial feet cooling-surface, and a weight of about 50 cwt. when empty and 100 cwt. when full.

Preparation of Pure Benzene, Toluene, etc.

The aniline colour-works require almost absolutely pure benzene and toluene, boiling within 0°.3 to 0°.5. These products were formerly mostly prepared at the colour-works, but they are now, especially in Germany, also made by the large tar-distillers, and this no doubt will gradually become more general, although the colour-works will always do some work in this line.

Such pure products can be obtained by means of rectifying-columns similar to those described on pp. 922 *et seq.;* but even then they contain slight quantities of aliphatic hydrocarbons, bases, carbon disulphide, and thiophen, although most of these can be removed as "fore-runnings" from the benzol still. Biehringer (*Dingl. polyt. J.*, cclxxvi., p. 78) found in such fore-runnings 57·3 per cent. CS_2, 7·49 per cent. nitriles, and small quantities of aldehydes and ketones. These, together with thiophens, are removed by repeated treatment with 2 or 3 per cent. concentrated or fuming sulphuric acid.

Removal of Sulphur Compounds.

Carbon disulphide (the discovery and quantitative estimation of which in benzol will be described *infra*) seems to have been first found in commercial benzol by Vincent and Delachanal (*Comptes rend.*, lxxxvi., p. 340). Most of it occurs in commercial 90 per cent. benzol, but even in "pure benzene," as it was sold at that time, Liebermann and Seyewetz (*Ber.*, 1891, p. 788) found 0·2 to 0·3 per cent. CS_2 by their own test. Weger (*Z. angew. Chem.*, 1909, p. 339) states that the average contents of carbon disulphide in the great majority of samples of 80/81 benzol is 0·1 to 0·2 per cent. Spilker (*Chem. Zeit.*, 1910, No. 76) states that the sulphur contents in commercial 90 per cent. benzol really exceeds 0·4 per cent. It is mostly present in the form of carbon disulphide, with a little thiophen. In crude benzol he found up to 0·8 per cent.

sulphur. Schwalbe (*Z. Farb.- u. Text.- Chem.*, 1905, p. 113; *Fischer's Jahresber.*, 1906, ii., p. 27) found in the purest commercial benzols 0·01 to 0·04 per cent. sulphur, in the form of carbon disulphide and thiophen.

Watson Smith (priv. comm.) has observed in English benzols up to 5 per cent. carbon disulphide, which gave rise to frequent complaints. The occurrence of this substance is easily accounted for, all conditions for its formation being present in the gas-retorts, viz., red-hot carbon and vapour of sulphur (from the pyrites which always occurs in coal); neither do the ordinary purifying agents, viz., sulphuric acid and alkali, remove it. It is true that a good deal of the carbon disulphide existing in raw tar will remain uncondensed during the distillation; but some of it must pass into the lightest oils, and all the more will pass, the more perfect the condensing-plant is. Its smell does not betray it, even when 20 per cent. is mixed with benzol, which is much in excess of anything ever occurring in practice. Five per cent. CS_2 in benzol makes no difference whatever in the smell; and even the first distillate smells of benzene, not of CS_2. But a safe test is afforded by the specific gravity, which is much raised by CS_2. Watson Smith, on adding 5 parts of CS_2 to 100 of benzol of sp. gr. 0·875, yielding 20 per cent. below 100°, got on distilling 35 per cent. below 100° of sp. gr. 0·917. By employing a Linnemann's fractionating apparatus or the like, probably nearly pure CS_2 would have been obtained.

The carbon disulphide is removed almost entirely in the "first runnings" by careful distillation; the last traces can be kept back by heating with an alcoholic solution of caustic potash, and removing the potassium xanthogenate formed thereby by washing. This process answers very well also on the large scale (Kraemer).

Thiophen and its homologues are mostly found even in "chemically pure benzene," as understood in the trade. They are very troublesome in the manufacture of products from benzol. Bidet (*Monit. Scient.*, 1889, p. 487) found that they cause in nitrobenzene and nitrotoluene a yellow colour, becoming more developed by contact with air. Aniline and toluidine made from such materials, show the same behaviour, whilst that made from material free from thiophen stands the light and has a much more pleasant smell. Hence aniline-colour makers have every reason to lay stress on the absence of thiophens in coal-tar oils. The tests for it will be described later on.

Really pure benzene is made from the article boiling between 80° and 82°, by allowing it to crystallize in a freezing-mixture, and separating the crystals from the mother-liquor by pressing, or by a centrifugal machine. This operation should be repeated once or twice. In order to remove the thiophen, this benzene must be agitated with renewed quantities of strong sulphuric acid till it ceases to give the blue reaction with isatin. Willgerodt (*J. prakt. Chem.* [3], xxxiii., p. 479) asserts that it can be purified by treating with chlorine-water. Haller and Michel (*Bull. Soc. Chim.* [3], xv., p. 390) obtain benzene quite free from thiophen by boiling it with 0·5 or 1 per cent. anhydrous aluminium chloride, washing with soda, and distilling. According to Boedtker (*Comptes rend.*, cxxiii., p. 310), in this case H_2S is formed, a molecular condensation of thiophen and benzene taking place with formation of a liquid boiling at upwards of 300°. But Heusler (*Berl. Ber.*, 1896, Ref. p. 656) ascribes the formation of this liquid to the action of $AlCl_3$ on non-saturated hydrocarbons.

Aluminium chloride, in the manner described above, is commercially employed by the Société anonyme des matières colorantes de St Denis (Ger. P. 79505). The benzene is heated with 0·5 per cent. $AlCl_3$ for several hours, decanted from the tarry matter which subsides on cooling, washed with sodium carbonate, and distilled. A similar process is that of Adiassewich (Ger. P. 83494).

Lippmann and Pollak (*Chem. Zentr.*, 1902, ii., p. 737) show that chloride of sulphur at 100° C. does not act upon pure benzene, but all thiophen is removed if the benzol is heated with 15 per cent. sulphur chloride on the water-bath for 192 hours, then distilled by steam, washed with alkali, and dried with calcium chloride (such a treatment is evidently too expensive for technical purposes).

Daub (Ger. P. 123053) purifies benzol from sulphur compounds by treating its vapour with carbon monoxide. Witzek (*J. Gasbeleucht.*, 1903, p. 85) points out that thiophen is just very stable at high temperatures! Daub's patent lapsed already after twelve months.

Schwalbe (Ger. P. 133761) removes CS_2 from benzol by moist ammonia gas, and thereupon thiophen by a mixture of sulphuric and nitric acids. The cost is stated = 6d. per 100 kg.

Donath and Ditz (*Chem. Zentr.*, 1900, i., p. 325) state that they remove both CS_2 and thiophen from benzol by treating it with alkaline permanganate solution at a higher temperature; but Russig states that this does not act on thiophen.

Ellerton (*J. Gas Lighting*, 1912, cxvii., p. 222) has tried to take the thiophen out of benzol by various reagents. Ozone, hydrogen peroxide, and plumbic oxide did not answer the purpose. Better results were obtained by washing the benzol with sulphuric acid. Of the 1·22 per cent. thiophen present in the unwashed benzole, sulphuric acid of 169° Tw. (8 per cent. of the benzol) left from 0·23 to 0·59 per cent.; fuming oil of vitriol (sp. gr. 1·87) from 0·22 to 0·27 per cent. in the benzol. The loss of benzol by this treatment amounted to 8 to 12 per cent., sometimes even more.

The Badische Anilin- und Sodafabrik (Ger. P. 211239) purifies the benzol hydrocarbons from thiophen and its homologues by treating them with an aldehyde or an organic acid anhydride, especially with formaldehyde, acetaldehyde, or phthalic anhydride, with addition of a suitable condensing agent. The purified hydrocarbons are separated from the condensation products by fractional distillation, blowing over by steam or in any other suitable way. As condensation agent, in the case of the aldehydes, moderately diluted sulphuric acid, in that of phthalic anhydride, aluminium chloride can be employed. Examples: 10,000 parts benzol, containing thiophen, is agitated with a mixture of 1500 parts sulphuric acid of 73 per cent. and 45 parts of 30 per cent. formaldehyde at the ordinary temperature for several hours; or, under the same conditions, 390 parts dried benzol with 7·5 parts formaldehyde and 7 parts anhydrous aluminium chloride. Up to that time, for economical reasons, the removal of the thiophen in technical practice had been only effected by treatment with sulphuric acid or aluminium chloride. But sulphuric acid effects the complete removal of thiophen only by several treatments; and aluminium chloride requires the application of higher temperatures, and of quite special methods of proceeding. On the contrary, the just described new process effects a very good purification, without practically acting upon the benzol, if the conditions of working are moderated to such an extent that the thiophen is acted upon; but the benzol, which under more energetic working conditions would also act with the substances added, remains intact. Together with the thiophen some alien hydrocarbons are also removed.

At the tar-works the process generally employed for removing the thiophen consists in agitating the benzol several times with 2 per cent. of fuming sulphuric acid, or 3 per cent. sulphuric acid of sp. gr. 1·84, during half an hour, and repeating this treatment until a sample is no more coloured by isatin-sulphuric acid (*vide* below). In order to obtain *chemically pure benzene*, the product obtained in the just stated way is cooled down to + 4° or + 5°, in order to *solidify* the benzene, and the liquid portions (toluene, etc.) are removed from the solidified benzene by suction or centrifugalling. This process (which has been already employed by A. W. Hofmann for preparing chemically pure benzene) must sometimes be repeated. According to G. Schultz (*Chemie des Steinkohlentheers*, 3rd ed., i., p. 31), chemically pure benzene, absolutely free from thiophen, can be obtained only by distilling benzoic acid, prepared from benzoic rosin or urine, with lime (1 part benzoic acid + 3 parts lime), removing the unchanged benzoic acid by shaking with caustic potash solution, driving the benzene over by steam, drying it by means of calcium chloride and sodium, and rectifying it, in order to remove benzophenon and diphenyl. In contrast with this (technically impossible) complication, Weger (*Z. angew. Chem.*, 1909, pp. 338 *et seq.*) states that chemically pure benzene, fulfilling all the conditions laid down *supra*, is manufactured from tar or coke-oven benzol, and is sent into the trade in truck-loads.

According to Witt (*Chem. Ind.*, 1887, p. 9; 1894, p. 31), at the aniline works 0·5 to 1·0 per cent. nitric acid is generally added during the last purification of benzol, to destroy *cumarone* and *indene* (cf. *infra* the statement about removing paraffins and olefins from toluene by a similar treatment).

Toluol — Ordinary Impurities of Commercial Toluol.— Carbon disulphide does not occur in toluol, on account of the great difference in boiling-points. The ordinary impurities of commercial toluol are traces of benzene, xylene, paraffins, and thiotolene. The removal of the sulphur compounds from toluol is effected in the same way as described *supra*, in the case of benzol.

Pure Toluene.—Whilst it is possible to manufacture benzene sufficiently pure for the highest requirements of colour-makers by double rectification and additional sulphuric-acid treatment, the case is different with *toluene* and especially *xylene*. Here paraffins and olefins occur, boiling at the same temperatures as the above, which go along with the nitro- and amido-products, and can be recognized in the latter as a turbidity on dissolving in dilute hydrochloric acid. On the small scale, these aliphatic hydrocarbons can be removed in the shape of resinous matters by boiling with sodium. On the large scale, this is done by agitating with hot sulphuric acid containing nitric acid. Thus the thiophens are destroyed, the olefins polymerized, and the paraffins after nitrification can be blown off by steam. Toluene and xylene purified in this way yield much more amides by nitration and reduction than the formerly worked impure hydrocarbons.

Friswell (*Chem. News*, 1893, lxviii., p. 27; *J. Soc. Chem. Ind.*, 1893, p. 589) mentions that at that time much toluene obtained from oil-gas occurred in trade, containing a large quantity of paraffins, which in toluene are even more injurious than in benzene. They are not indicated by the boiling-points, but by shaking the toluene with the same volume of sulphuric acid, sp. gr. 1·84. [Real paraffins are not dissolved or changed by sulphuric acid, but no doubt non-saturated hydrocarbons are understood.] In the case of *pure* toluene the layers separate at once; the acid is colourless or faintly brown, and remains so for twenty-seven hours. With impure toluene, emulsions are formed separating only after five or ten minutes; the acid takes a bright orange colour, after an hour turning green at the top, after twenty-four hours altogether green or black. Whilst it is usual to remove the impurities by strong sulphuric acid or even by Nordhausen oil of vitriol in which case much toluene is converted into sulphonic acid, Friswell recommends on the latter account less concentrated acid, viz., 10 volumes per cent. sulphuric acid, sp. gr. 1·84, to be agitated for four hours; after settling and drawing off the acid, the oil is at once washed with caustic-soda liquor. The loss does not exceed 5 per cent., and consists half of paraffins. Some toluenes require more energetic treatment than others. After washing they are rectified and leave behind polymerized bodies of 260° to 285° boiling-point. The waste acid, in order to be recovered, must be separated by dilution from a dark green oil, which, if almost free from acid, is soluble in water.

Toluene can be obtained directly from coal-gas (*vide supra*, p. 81), which contains from twenty to forty times the amount of toluene per ton of coal carbonized than is furnished by the tar produced from the same bulk. According to *Chem. Trade J.*, 1915, lvi., p. 164, it has been proved that the toluol can be washed out of the gas, replacing it, if necessary, by benzol to preserve the illuminating and calorific value of the gas. Experiments conducted at Birmingham have shown that pre-benzolizing the wash-oil by 5 per cent. renders it possible to extract nearly 80 per cent. of the toluol content, and still leave more than 65 per cent. of the benzol content in the gas. Two lb. of pure toluene should be easily recoverable from 10,000 cub. ft. of coal-gas. The principal use of pure toluene is for the manufacture of trinitro-toluene.

The supply of toluene (which is the raw material for the manufacture of very important explosives) was discussed by Macintosh Williams, speaking on behalf of the British War Office Committee on the Supply of High Explosives, and W. B. Davidson, in February 1915, at a meeting of representatives of the Gas Industry (*J. Gas Lighting*, 9th and 16th Feb. 1915). It was suggested to saturate the wash-oil, employed for scrubbing the gas at gas-works, with benzol, about 5 per cent. by volume, which would cause the oil to take up only the toluol contents of the gas, and leave the benzol contents of the gas to a certain extent intact. It is possible by this proceeding to extract nearly 80 per cent. of the toluene, and to leave over two-thirds of the benzol in the gas. The toluol thus obtained is redistilled in a Heckmann or Savalle still (*supra*, pp. 927 and 934).

Pure Xylenes.—As we have seen on page 234, xylol is found in trade in three forms—crude xylol, purified xylol, and "pure xylene." The difference between crude and purified xylol is merely this: that the upper limit of boiling-points in the case of the latter is a trifle less (5 per cent.) than in that of crude xylol;

that the purified xylol must be of water-white colour, and must satisfy certain requirements concerning the reaction with sulphuric acid and the titration with bromine (see below).

This is brought about by washing it more carefully than the crude xylol. Both of them contain a considerable proportion of toluol, as is best proved by the fact that according to the requirements of trade the *lower* limit of boiling is fixed at 120°, whereas the boiling-points of the isomeric xylenes are *p*-xylene 138°·5, *m*-xylene 140°, and *o*-xylene 142° (corr. according to Weger).

What the tar-distillers and benzol-rectifiers sell as *pure xylene* is a mixture of the three isomeric xylenes, with the limitation that 90 per cent. must boil within 3°·6 and 95 per cent. within 4°·5, so that the total fraction of the xylenes is cut out pretty sharply within the limits from 138° to 142°. The sp. gr. of this fraction is 0·86 and its flashing-point about 21°. That mixture contains about 60 per cent. of the more valuable *m*-xylene, 10 to 25 per cent. of *o*- and 15 to 30 per cent. *p*-xylene, with a little ethyl-benzene and very little trimethyl-benzenes, paraffins, and thioxen (Weger).

Purification of Xylol.—Before isolating the three isomers, the mixture must be separated from the most essential impurities—aliphatic hydrocarbons, thioxen, and ethyl-benzene. The aliphatic hydrocarbons and the thioxen can be easily removed by the processes described in the analogous cases of benzene and toluene. Ethylbenzene can be removed, according to Friedel and Crafts (*Comptes rend.*, 1892, cxii., p. 1110), by treating with bromine, twenty times the weight of the oil, and a little iodine; but this of course is not a technical method.

Separation of the Three Isomeric Xylenes.—This operation is up to the present usually not carried out by the tar-distiller, but by the aniline-colour manufacturer. We shall quote the more important methods for manufacturing purposes.

Reuter (*Chem. Zeit.*, 1889, pp. 830 and 850) indicates the following method as applicable to separating the three isomeric xylenes on a large scale. Sulphuric acid of more than 80 per cent. H_2SO_4 acts on metaxylene, but para- and orthoxylene are not acted upon by acid below 84 per cent. If the ordinary strong acid of 93 to 95 per cent. is employed, metaxylene is acted upon until the proportion of water to real acid attains 20:80, but for the other isomers 16:84. Hence an acid saturated with metaxylene can be mixed with $\frac{1}{8}$ of its weight of fresh acid without dissolving para- or orthoxylene. The crude xylol (which ought not to boil below 136°, 90 per cent. passing over up to 145°) is washed several times with small quantities of sulphuric acid, in cast-iron pans with agitators at a temperature not exceeding 80° C., in which case only metaxylene is converted into sulphonic acid. This is secured by employing just the proper quantity of acid, as found in a preliminary trial made with a kilogram of the xylene. The solution containing 2 or 3 per cent. mechanically dissolved paraffins and terpenes is freed from these by dilution to 1·4 sp. gr., avoiding a rise of temperature above 100°. After separating the oil rising to the top, the mass is allowed to cool, when most of the α-metaxylenesulphonic acid crystallizes out. From this *metaxylene* is quantitatively regenerated by heating at 220° with water in an autoclave, or by dry distillation of the ammonia salt, 80 or 90 per cent. being thus recovered.

From the oils separated from the metaxylenesulphonic acid, the *paraxylene* is recovered by treating them with an *excess* of sulphuric acid at 80° C., and treating the acid liquid as above described. The paraxylenesulphonic acid is purified by recrystallization, and the hydrocarbon is quantitatively recovered by decomposition with water in an autoclave (dry distillation of the ammonia salt yields only about 20 per cent.).—The *orthoxylene* remains in the mother-liquor from the paraxylenesulphonic acid, and is obtained by converting the sulphonic acid into the calcium salt, then into the sodium salt, acidulating this, and treating the free sulphonic acid as in the case of paraxylene.

Somewhat similar to Reuter's process is that of Crafts (*Comptes rend.*, cxiv, p. 1110). Börnstein and Kleemann (Ger. P. 56322; *Berl. Ber.*, 1891, Ref. p. 486) first convert the xylene mixture into xylidines, and separate these by means of sulphur dioxide, which forms crystalline compounds with ortho- and metaxylene, leaving paraxylene in the liquid state. Of course this process can be thought of only where the xylidines themselves are wanted, that is in the aniline-colour works.

Nearly pure metaxylene, which is sometimes required for technical purposes, can be made by the following process, communicated to me by Dr C. Häussermann. Ordinary xylol, which contains but little orthoxylene, is first agitated with 5 per cent. of its weight of strong sulphuric acid, in order to remove the thio-compounds, and is then converted into sulphonic acids, by agitating with its own weight of sulphuric acid, sp. gr. 1·84, for several hours. The acid solution is separated from the undissolved portion, and is then treated with a current of steam (as indicated by Armstrong for decomposing sulphonic acids). The metaxylene distilling over needs only to be freed from acid, in order to be worked up at once for metaxylidine. All these operations can be carried out on the manufacturing scale without any difficulty.

Levinstein's method for separating the three isomers of xylene in the laboratory for analytical purposes will be described later on.

Weger (*loc. cit.*) indicates the following process for separating the three isomeric xylenes. First the most easily isolated, the *m*-xylene, is prepared according to Reuter's above-described process by means of 80 per cent. sulphuric acid. The remaining mixture of *o*- and *p*-xylene is well fractionated in a properly acting column-apparatus (*vide* pp. 923 *et seq.*). The boiling-points of these two components are now 4° apart from each other. *p*-xylene crystallizes at +15°, and can therefore be obtained by several times cooling the mixture and removing the portion remaining in the liquid state, if a crude *p*-xylol is at disposal, which solidifies by moderate cooling.

Yields of the Various Commercial Products obtained in Working-up the Light Oil and Crude Naphtha.

These yields differ in pretty wide limits, depending on the quality of the coals carbonized, and on the processes employed for utilizing them. On the whole gas-tars are richer in benzol and its homologues than coke-oven tars.

In the year 1891 Kraemer estimated the yield of tar in the German *coal-gas* industry at 2·5 per cent. of the coal. Since then important changes have taken place, both in the quantity and in the composition of the tar, owing to the introduction of new types of furnaces for the purpose of increasing the yield of illuminating-gas. We quote here two examples of results obtained during recent years at German *gas-works* from 100 parts of coal.

	I.	II.
	Per cent.	Per cent.
90 per cent. benzol	0·84 to 1·10	0·68 to 0·87
Toluol	0·09 „ 0·11	0·20 „ 0·28
Heavy benzol (solvent naphtha, etc.)	0·36 „ 0·87	0·43 „ 1·46
	1·29 „ 2·08	1·31 „ 2·61
Average . . .	1·68	1·96

The following are examples of the results from working-up *coke-oven tars* :—

	Tar from		
	Westphalian coal. (Pluto pit.)	Upper Silesian coal. (Otto-Hofmann ovens.)	Saar coal (Heinitz pit.)
	Per cent.	Per cent.	Per cent.
Benzol	0·21	1·1 to 1·2	1·75
Toluol		0·24	
Solvent-naphtha, I. . . .	0·09	0·30	1·50
„ „ II. . . .	0·47		

Supra (p. 116), we have quoted the results obtained by C. Otto when gasifying the same description of coal—(1st) in ordinary gas-retorts, (2nd) in Otto-Hofmann coke-ovens. We here repeat the most salient figures to illustrate our present purpose. The tars obtained by the two classes of processes yielded :—

	Tar from Gas-retorts.	Tar from Coke-ovens.
	Per cent.	Per cent.
Light oil up to 200°	4	3·4
And from this, calculated on the tar :		
Aniline benzols	0·92	1·1
Solvent-naphtha	0·20	0·32
Total . . .	1·12	1·42

Häussermann (priv. comm.) regularly obtains a yield of 70 parts of pure benzene from 100 parts of 90 per cent., and 45 to 48 pure benzene from 100 parts of 50 per cent. benzol by means of a Savalle's column.

Cf. also the results of Coupier, p. 922 *et seq.*

English coke-oven tars, from Simon-Carvès ovens (*supra*, p. 119), using various descriptions of coal, yielded the following results:—

	Pease's pit (Sadlor).	Bear-park pit (Watson Smith).	
	a.	*b.*	c.
Light oil . .	4·5 per cent.	5·12 per cent.	5·12 per cent.

The working-up of these tars yielded (calculated on 100 parts tar):—

	a.	*b.*	*c.*
	Per cent.	Per cent.	Per cent.
50/90 per cent. benzol	0·50	0·703	...
Benzol boiling from 80° to 100° . . .	...	...	0·53
Toluol boiling from 100° to 120° . .	...	...	0·29
Solvent naphtha 90 per cent. up to 150° .	0·60	1·031	1·25
Burning-naphtha	0·40	0·434	0·20
	1·50	2·168	2·27

These tars are decidedly of the same quality as good gas-tars, and contain only slightly less benzol, toluol, and xylol.

The yields of the various commercial benzols from *light oil* differ as much with the conditions under which the light oil has been obtained that no generally valid statements can be made thereon.

According to Kraemer and Spilker (*loc. cit.*, p. 16) normal light oil contains about 80 per cent. aromatic hydrocarbons, 64 per cent. of which are benzol and its homologues, and 16 per cent. naphthalene. These 64 per cent. consist of:

Benzene	41·5	per cent.
Toluene	12·5	"
Xylenes	6·0	"
Solvent-naphtha (tri- and tetra-methyl benzenes)	4·0	"
	64·0	"

The *crude benzol* from coke-oven tar, according to Rau (*loc. cit.*) contains:

90 per cent. benzol	about 70 per cent.
Toluene	„ 16 „
Xylenes	„ 8 „
Solvent-naphtha	„ 10 „

The following statements give the yield of *pure hydrocarbons* from commercial products.

G. E. Davis (*J. Soc. Chem. Ind.*, 1885, p. 648) finds in 90 per cent. and 50/90 per cent. benzol:—

	90 per cent.	50/90 per cent.
Pure benzene	75	50
„ toluene	24	40
„ xylene	1	10

Schultz quotes the following yields, as obtained by a rectifying-column:—

	From 50 per cent. benzol.	From 90 per cent. benzol.
Fore-runnings up to 81°	5 to 10	10 to 27
Pure benzene	30 „ 40	65 „ 75
Benzol for red	5	10
Pure toluene	35 „ 40	2 „ 4
Xylenes	5 „ 8	

Composition and Properties of the Commercial Descriptions of Benzol and Naphtha.

The demands made upon the qualities to be exhibited by commercial benzols and naphtha vary, of course, according to the purposes for which they are to be employed. The conditions laid down for that purpose embrace the fractions to be obtained by distillation at certain boiling-points, the specific gravity, the behaviour towards sulphuric acid and bromine, the amount of paraffins, thiophen, and carbon disulphide, the colour and the smell (the last-named especially in case of the higher-boiling products).

The distillation of the products from light tar-oils in the laboratory, carried out in the manner described later on in this chapter, yields the following distillates (in percentages by volume), according to my own tests:—

Commercial products.	Initial boiling-point.	88°.	93°.	100°.	110°.	120°.	130°.	138°.	149°.	160°.	171°.
90 per cent. benzol .	82°	30	65	90	...	...	...	...	...	...	...
50 per cent. benzol .	88°	...	13	54	74	90	...	...	...	...	...
Toluol . . .	100°	...	...	...	56	90	...	...	...	...	...
Carburetting-naphtha .	108°	...	...	...	1	35	71	84	97	...	...
Solvent-naphtha . .	110°	...	...	...	...	17	57	71	90	...	...
Burning-naphtha . .	138°	...	...	...	...	...	...	...	30	71·5	89

The temperatures were all measured with the thermometer-bulb just submerged in the liquid, at the beginning of the distillation.

Häussermann (*Industrie der Theerfarbstoffe*, pp. 13 and 14) quotes the following percentage results:—

At . . .	85°.	90°.	95°.	100°.	105°.	115°.	120°.	135°.	140°.	145°.	150°.	170°.	180°.
90 per cent. benzol	20	72	84	95	95	98	...	...	...	...	...	...	...
50 per cent. benzol	...	5	30	50	64	81	94	...	...	...	...	...	...
Solvent-naphtha .	...	...	...	...	...	...	...	6	48	72	85	92	95

According to a statement, made to me by an English tar-distiller, the ordinary results are *per cent.*:—

At . . .	100°.	120°.	130°.	160°.	Sp. gr.
90 per cent. benzol . . .	90	...	...	...	0·885
50 per cent. benzol . . .	50	90	...	...	0·880
30 per cent. benzol . . .	30	90	...	...	0·875
Solvent-naphtha	...	...	20	90	0·875
Burning-naphtha	...	...	...	30	0·885

Hohenhausen quotes:—

Benzol.					
90 per cent. Sp. gr. 0·882.		50 per cent. Sp. gr. 0·878.		30 per cent. Sp. gr. 0·875.	
	Per cent.		Per cent.		Per cent.
At 83°	5	At 94°	10	At 97°	12
85°	22	95°	18	98°	21
88°	62	98°	40	100°	30
90°	74	100°	50	105°	55
92°	81	105°	68	110°	73
95°	87	110°	79	115°	84
100°	90	115°	85	120°	90
105°	94	120°	90		
110°	98				

Schultz (*cf.* also his results, p. 948) quotes:—

At . .	85°.	90°.	95°.	100°.	105°.	110°.	115°.	120°.
90 per cent. benzol .	25	70	83	90	94	97	98	99
50 per cent. benzol .	0	4	26	50	62	71	82	90
30 per cent. benzol .	0	2	12	30	42	70	82	90

In Germany the "benzols" are designated by Roman numbers, and correspond approximately to the English designations as follows:—

Benzol No. I. to English 90 per cent. benzol.
„ II. „ 50 per cent. „
„ III. „ toluol (in Germany: 0 per cent. benzol).
„ IV. „ carburetting naphtha.
„ V. „ solvent-naphtha I ("Lösebenzol").
„ VI. „ solvent-naphtha II („).

"Heavy benzol" of commerce to burning-naphtha.

The percentages which these various grades yield on distillation are given by Kraemer and Spilker as follows:—

Up to Degree Centigrade per cent.

Benzol. No.	85°	90°	95°	100°	105°	110°	115°	120°	125°	180°	135°	140°	150°	160°	170°	180°	190°
I. . .	48	78	87·5	91·5	...	...	...	...	...	...	...	...	...	...	...	...	...
II. . .	...	3	31·0	52·0	67	77	84	90	...	...	...	...	...	...	...	...	...
III. . .	...	...	...	...	11	49	79	91	95	...	...	...	...	...	...	...	...
IV. . .	...	...	...	...	...	...	...	...	...	30	60	87	...	...	...	...	...
V. . .	...	...	...	...	...	...	...	...	...	...	...	20	75	91	...	...	...
VI. . .	...	...	...	...	...	...	...	...	..	...	...	...	5	50	84	...	...
Heavy benzol	...	...	...	...	...	...	...	...	...	...	...	...	...	...	45	82	91

The real average composition of commercial benzols has been found by Kraemer and Spilker, as the result of very numerous tests, to be as follows:—

	Benzene.	Toluene.	Xylenes.	Cumenes.	Neutral naphthalene oils.
Benzol No. I. (so-called 90 per cent.) .	84	13	3	...	...
" II. (so-called 50 per cent.) .	43	46	11	...	...
" III. " " .	15	75	10	...	...
" IV. " " .	...	25	70	5	...
" V. (solvent-naphtha—160°) .	...	5	70	25	...
" VI. (" " —175°) .	...	...	35	60	5
Commercial "heavy benzol" . . .	...	...	5	80	15

The last column ("neutral naphthalene oils") signifies the liquid companions of solid naphthalene, comprising much naphthalene, tetra-, penta-, and hexymethylated benzenes and other hitherto hardly known compounds. The above table does not take account of impurities, but only of the benzol hydrocarbons. The following statements of the same authors quote the average composition of the products, obtained during six months at a large tar-works:—

[TABLE

	90 per cent. commercial benzol.	50 per cent. commercial benzol.	Commercial benzol, No. III.
	Per cent.	Per cent.	Per cent.
Water	0·060	...	...
Paraffins	0·100	0·25	0·50
Carbon disulphide	0·086	0·39	...
Substances adding bromine, inclusive of thiophenes	1·202	1·23	0·82
Benzene	80·922	45·37	13·54
Toluene	14·850	40·32	73·42
Xylenes	2·180	12·14	11·69

Kraemer and Spilker point out that the proportion in which the benzol hydrocarbons occur in the commercial grades of benzol may show considerable differences, and that the just given tables do not exhibit the constant composition, but merely the average values of commercial products. They found, for instance, that the requirements laid down for the boiling limits of "90 per cent. benzol" are fulfilled by every one of the following artificially prepared mixtures, only the last of which exhibits the composition of normal 90 per cent. benzol:—

1. 82·0 per cent. benzene + 18 per cent. toluene.
2. 92·2 " " + 7·8 " xylene.
3. 90·0 " " + 5·0 " toluene + 5·0 per cent. xylene.
4. 82·0 " " + 15 " " + 3·0 " "

Besides these types, small quantities of "Cumol" and "Pseudocumole" are found in the German trade, where also the types of "30 per cent." and "0 per cent." benzol understanding by "per cent." the quantities distilling up to 100° C., are met with.

Recently, by the name of "Technisches Benzol," a product is coming into the German market, consisting of about 95 per cent. real benzene + 5 toluene, and yielding on distillation at least 90 per cent. up to 90° C.

Another classification, employed by the German Union of Benzol Manufacturers, runs as follows:—

Designation.	Boiling-point (° C.).	Colour.
90 per cent. crude benzol	90 to 93 per cent. up to 100°	...
Purified 90 per cent. benzol	90 to 93 per cent. up to 100°	water-white.
Purified 50 per cent. benzol	50 per cent. up to 100°; 90 per cent. up to 120°	water-white.
Pure benzol	90 per cent. within 0°·6; 95 per cent. within 0°·8	water-white.
Crude toluol	90 per cent. between 100° and 120°	...
Purified toluol	90 per cent. between 100° and 120°	water-white.
Pure toluol	90 per cent. within 0°·6; 95 per cent. within 0°·80	water-white.
Crude xylol	90 per cent. between 120° and 150°	water-white to yellowish.
Purified xylol	90 per cent. between 120° and 145°	water-white.
Pure xylol	90 per cent. within 3°·6; 95 per cent. within 4°·5	water-white.
Crude solvent-naphtha	90 per cent. within 150° and 180°	...
Purified solvent-naphtha, No. I.	Not less than 90 per cent. up to 160°	water-white to faintly yellow.
Purified solvent-naphtha, No. II.	Not less than 90 per cent. up to 175°	...
Heavy benzol	Boiling below 200°	...

Allen (*Commercial Organic Analysis*, ii., p. 87) gives the following results of distilling the commercial products in the usual way:—

	Very good first runnings (once-run naphtha).	Good 90 per cent. benzol.	Scotch 90 per cent. benzol.	50/90. per cent. benzol.	80 per cent. benzol.	Solvent-naphtha.	Mixture of 70 pure benzene and 80 toluene.
Spec. grav.	...	0·882	0·883	0·880	0·875	0·877	0·880
	Degrees.	Degrees.	Degrees.	Degrees.	Degrees.	Degrees.	Degrees.
First drop collected at	...	82	...	...	...	...	85·4
10 per cent. "	96	83¾	84½	94	97	128½	86·6
20 " "	99½	84½	85	95	98	130	87·2
30 " "	102	85	85¾	96½	99½	132½	87·8
40 " "	107	85¾	86½	98	101	135	88·8
50 " "	111	86¾	87¼	100	104	137	89·8
60 " "	119	88	89	102½	106	140	91·4
70 " "	128	89¾	91¼	106	109½	143½	93·2
80 " "	145	92½	94¾	110½	113½	148½	96·2
90 " "	170	...	...	120	120	156	102·6
92 " "	...	100	...	...	...	...	...
95 " "	...	...	...	...	...	...	107·0

According to the same author, a good sample of *90 per cent. benzol* should not begin to distil under 80° and should not yield more than 20 to 30 per cent. at 85°, or much more than 90 per cent. at 100°. An excessive distillate, *e.g.*, 35 to 40 per cent. at 15°, indicates a larger proportion of carbon disulphide (see below) or light hydrocarbons than is desirable. The actual percentage composition of a 90 per cent. benzol of good quality is about 70 per cent. of benzene, 24 of toluene, a trace of xylene, and 4 to 6 of carbon disulphide and light hydrocarbons. It should be colourless and free from opalescence. The specific gravity of English 90 per cent. benzols usually ranges from 0·880 to 0·888 at 15°·5; that of Scotch benzols (which contain little carbon disulphide, but a considerable proportion of light hydrocarbons) is often as low as 0·871. *Fifty to ninety per cent. benzol* (50/90) is a product of which 50 per cent. by volume distils over at a temperature not exceeding 100°, and 40 per cent. more below 120°. *Thirty per cent. benzol* yields 30 per cent. at 100°, and 60 per cent. more between 100° and 120°; it consists chiefly of toluene and xylene. *Solvent-naphtha* gives from 8 to 30 per cent. distillate below 130°, and about 90 below 160°; it consists chiefly of toluene and xylene, with notable quantities of cumene and still higher homologues, and several per cent. of naphthalene [to some of these statements I must demur; there can be but very little toluene in this product; and "cumene" does not occur in coal-tar at all, but only isomers of this body].

According to the same author (*loc. cit.*, 2nd ed., ii., p. 475) some contract-notes for Continental customers specify the following tests for commercial benzol:—1st, 1 c.c. is agitated with 20 c.c. of pure concentrated sulphuric acid and allowed to stand for some hours. The coloration at the end of this time should be very slight, never exceeding a pale straw-yellow. 2nd, 10 c.c. of the sample is agitated in a stoppered bottle with successive small quantities of saturated bromine-water, until a yellow tint is obtained which remains for some minutes. No more than 0·5 c.c. of bromine-water should be required to produce this result.

Hohenhausen quotes as usual *specific gravities* of English 30 per cent. benzol 0·875 at 15°, of 50 per cent. benzol 0·878, of 90 per cent. benzol 0·882. When the specific gravity is lower than 0·875, the presence of paraffin or non-nitrifiable hydrocarbons may be suspected. Most of the Scotch benzol has a lower specific gravity, on the average 0·870, and contains 7 or 8 per cent. of paraffins, some of it as low as 0·860 (Trewby).

Requirements laid down for the Properties to be exhibited by Pure Benzol and Pure Toluol sent into the Trade.

The following statements are made by Weger (*Z. angew. Chem.*, 1909, p. 339). "*Pure benzol*" of commerce (also designated as 80/81 per cent. or crystallized benzol) has a sp. gr. = 0·885 at 15°, fusing-point = 5°, and boiling-point = 80°·5. According to the rules of the German Benzol Union, of such "pure" benzol, 90 per cent. should pass over within 0°·6, 95 per cent. within 0°·8, and there should be hardly any colour produced by sulphuric acid. Such "pure benzol" still contains thiophen and carbon disulphide, as well as traces of toluene and paraffins. The quantity of thiophen which V. Meyer stated = 0·5 per cent. is in reality only about 0·15 per cent. (For details on this point and on the tests for thiophen, *cf.* Weger, *loc. cit.*) *Benzol free from thiophen* is also manufactured in Germany and sold in truck-loads; it is made by thorough washing with concentrated sulphuric acid. The average percentage of carbon disulphide in "pure benzol" is 0·1 to 0·2 per cent. Generally it is of no importance, but is troublesome in some analytical methods, where it may cause errors. It may be removed from the benzol by treating it with ammonia or with alcoholic potash. "Pure benzol" is employed for preparing nitrobenzene and benzene sulphuric acids, serving for the synthetical production of phenol and resorcin.

Pure toluene of commerce, according to a private communication from Dr Häussermann, ought to satisfy the following tests:—It should boil within 1°. When shaken up for some time with its own volume of strong sulphuric acid, it ought not to cause any coloration. On shaking up for some minutes 90 c.c. of toluene with 10 c.c. of nitric acid of sp. gr. 1·44 in a stoppered jar, the acid should assume only a red colour, and remain quite clear and bright, not turn greenish or blackish and thick. Some samples of toluene which answer to these tests still contain 0·5 per cent. of non-nitrifiable hydrocarbons, which may be troublesome on the large scale; these should be tested for, as will be described hereafter, but not less than 1 kg. of toluene ought to be employed for this test.

Pure toluol of commerce has the sp. gr. 0·872 at 15°, boils at 111°, and solidifies only at −90° C. According to the rules of the German Benzol Union, 90 per cent. should distil within 0°·6, 95 per cent. within 0°·8, and the sulphuric acid reaction should produce hardly any colour. It contains traces of benzene, xylenes, paraffin, and thiotoluene. The latter is found by Laubenheimer's reaction (blue-green colour with phenanthrenequinone, glacial-acetic acid, and concentrated sulphuric acid). Toluol free from thiotoluene can be also obtained in commerce.

The ordinary "pure toluol" is employed for the manufacture of trinitrotoluene (as an explosive agent), of toluidine, benzyl chloride, benzaldehyde (for artificial indigo), etc.

TESTING METHODS FOR LIGHT OILS (NAPHTHA) AND COMMERCIAL BENZOLS.

I. *Light Oil.*

Light oil is an article of trade, since it is sold by smaller tar-distillers, and by manufacturers of roofing-felt and asphalt, who are not in a position to work it up economically, to larger tar-distilling works.

The testing of light oil comprises the estimation of specific gravity and of the boiling-points of the crude oil, of the specific gravity of the fractions distilling to 120° and 160°, and of the percentage of phenols, bases, and naphthalene.

The *specific gravity* is usually estimated by means of a hydrometer or of Mohr's balance. It varies with the boiling-points; in the case of normal light oil which yields 90 per cent. distillates up to 200°, it is about 0·930. If oils, exhibiting the just named boiling-point, show a specific gravity below 0·900, or exceeding 0·960, this points to their being mixed with foreign oils, *e.g.*, distillates from oil-gas tar, or from the lignite and petroleum industry.

The *boiling points*, i.e., the limits of temperature between which the single fractions are collected, are in Great Britain usually determined in glass retorts; in Germany mostly in copper flasks, of a capacity of about 150 c.c., and connected by means of a tube in its top, fitted with a thermometer, with a Liebig condenser. For every test 100 c.c. are employed. The distillates are collected in graduated test-tubes, mounted on a turn-table, so that the single fractions can be collected without interrupting the distillation, in the same manner as will be described lower down for testing benzol. The distillation is carried on, until at least 95 per cent. of the sample have passed over. The total distillate up to 120° is tested for its specific gravity, which in the case of good light oil ought to be 0·880 to 0·885; if it is below 0·880, there is a suspicion of paraffins being present. The fractions distilling above 180°, when cooled down to the ordinary temperature, give a crystallization of *naphthalene*, the quantity of which is found by pressing between filtering-paper, or draining on porous earthenware plates.

In order to test for *phenols* and for *bases* (pyridines), all the fractions are united, rinsing out the graduated test-tubes with xylol, and the mixture is shaken in a graduated cylinder with 100 c.c. caustic-soda solution of sp. gr. 1·100. After the two liquids have separated by repose, the volume now occupied by the aqueous liquid (the caustic-soda solution) is read off. Every cubic centimetre over and above 100 is calculated = 1 per cent. of *phenols*. In order to estimate these more accurately, the caustic-soda solution is carefully separated from the oily layer and is boiled down on the water-bath, until there is no more cloudiness produced by the addition of water; it is then allowed to cool down, acidulated with hydrochloric acid, and salted out by addition of common salt. The volume of the phenols separated is read off and calculated = 1 per cent. per cubic centimetre.

The quantity of *bases* is found by shaking the oil, remaining after extracting the phenols as above, with 30 c.c. sulphuric acid of 20 per cent. H_2SO_4, allowing to settle, and measuring the increase of volume of the sulphuric acid. A controlling operation can be made by evaporating, as in the case of the phenols, and careful precipitation with a large excess of caustic-soda solution of sp. gr. 1·4. The quantity of *pyridine* present in the mixture of bases is determined by the process described in Chapter X., p. 854, and *infra*, p. 988.

The testing of light oil for the quantity of commercial products to be obtained by working them up on a large scale will be described lower down, in connection with the testing of crude benzol for commercial products.

II. *Commercial Benzols.*

The laboratory tests for the benzols bought and sold vary, of course, according to the demands of the trade. We shall describe them in detail; but of course not in every case all these tests are required. Those always made are the fractional distillation, the specific gravity, the behaviour towards sulphuric acid and bromine, the percentage of paraffins, carbon disulphide, and thiophen; in the case of the high-boiling benzols also the smell.

1. *Fractional Distillation.*

A test always performed is that by *fractional distillation.* For this purpose usually ordinary glass retorts or fractionating-bulbs are employed (see Fig. 181, p. 868). In this case the position of the thermometer is of great importance (p. 868), and also in other respects different results may be obtained in apparatus of unequal construction. On this account and owing to the fragile nature of glass retorts, Regnault (*Ann. Chim. Phys.*, lxviii., p. 409), at the instance of the French Government, constructed a *standard apparatus*, which is shown in section in Fig. 205. A is a cylindrical copper retort with a neck, *a*, and a bent vapour-tube, *b c*. The latter fits tightly into the lateral tube *d* of the condenser B. This consists of a brass cylinder, *e f*, ending at top and bottom in narrow metal tubes, *g* and *i*, and fixed air-tight in a wider metal cylinder, *m n*. Into the latter enters a stream of water through *o* at the bottom and leaves at the top at *p*. It stands on a tripod, P P, to which a horizontal frame, *h l*, is attached. In the latter slides a carrier, V, containing five glass tubes, closed at the bottom and divided into cubic centimetres; every one of the tubes can be thus brought under the outlet-pipe (*i*) of the condenser. By means of a pipette the retort is charged with

100 c.c. of benzol, which ought not to occupy much more than a third of it. The thermometer T is fixed in the neck *a*, so that its bulb does not dip into the liquid, and that the 80th degree comes out very little above the cork. The distillation is carried on by the gas- or alcohol-flame S. The ordinary fixed points for changing the receivers 1 to 5 are 100°, 120°, 140°, 160°, and 180°. The convenience of this arrangement for changing the receivers and reading off the volume of each fraction will be at once apparent. The condenser is cooled by means of water.

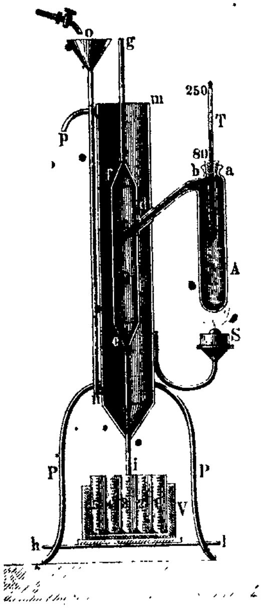

FIG. 205.

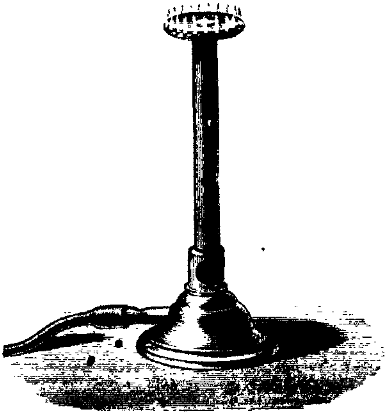

FIG. 206.

Herr (*Chem. Zeit.*, 1908, p. 148; *J. Soc. Chem. Ind.*, 1908, p. 217) describes another kind of dephlegmator. This is a glass tube, 300 to 1000 mm. long, filled with lead shot-bullets, six of which weigh 1 g. The cylinder is covered with cotton-wool or the like, to prevent loss of heat. Further arrangements are described by means of which it is possible to fractionate liquids at temperatures up to 330° C., such as petroleum.

English Method.—At the English tar-works and at the buyers' laboratories glass retorts are employed for testing benzol. Frequently differences of opinion occur between buyer and seller, chiefly caused by the fact that it is not usual in the English trade to place the thermometer in the only proper position, as shown in the diagram, Fig. 181, p. 868, but to let it dip more or less into the liquid. Further deviations are caused by differences in the size of the retorts and the speed of the distillation. The following detailed directions, by W. W. Staveley (*Chem. News*, xliii., p. 70), are intended to produce a uniform result; but this would involve their being accepted everywhere as binding, which is far from being the case. One hundred c.c. of the sample is to be put into an ordinary 6-oz. stoppered retort, connected with a Liebig's condenser whose condensing-tube is 1 in. wide and 30 in. long. The thermometer is so fixed that its lowest point is ⅜ in. from the lowest portion of the retort. Heat is applied by means of a Bunsen rose-burner (Fig. 206), in such a manner that the distillate runs in separate drops into the 100 c.c. burette employed as the receiver. A moment before the desired temperature is reached the lamp is removed, whereupon the thermometer rises to the proper point; and the reading-off is made as soon as the benzol has ceased to drop from the condensing-tube. The contents of the retort, after cooling, are poured into the burette; and the loss, if any, is added to the percentage of the distillate. New corks absorb benzol, and hence are not to be recommended; neither are new clean retorts suitable, unless a few fragments of brick are introduced. Best of all are retorts which, having been used for some time, have a slight coating of carbon inside.

Some years ago I found at the largest English tar-works 8-oz. retorts, whose beaks dipped into condensing-tubes ⅞ in. wide and 27 in. long, surrounded by a glass cooler, as shown in Fig. 207. The thermometer was so placed in the retort that its end was ⅜ in. from the bottom.

Allen (*Comm. Org. Anal.*, 2nd ed., ii., p. 496), in contradiction to the numerous complaints respecting the uncertain results of the ordinary English commercial-benzol testing, asserts that very constant results can be obtained by different operators, the variations rarely exceeding 1 or 1½ per cent. if the test is properly understood. He gives the following instructions for conducting the ordinary retort-test, so as to ensure results as accurate as the process will admit of. They apply to 90 per cent. benzol, which must, of course, be modified to suit other qualities. One hundred c.c. of the benzol is measured in an accurately graduated cylinder, and poured thence into a tubulated retort holding 200 c.c., or 8 fluid ounces. A delicate thermometer, 14 in. long and with a small bulb, is fixed in

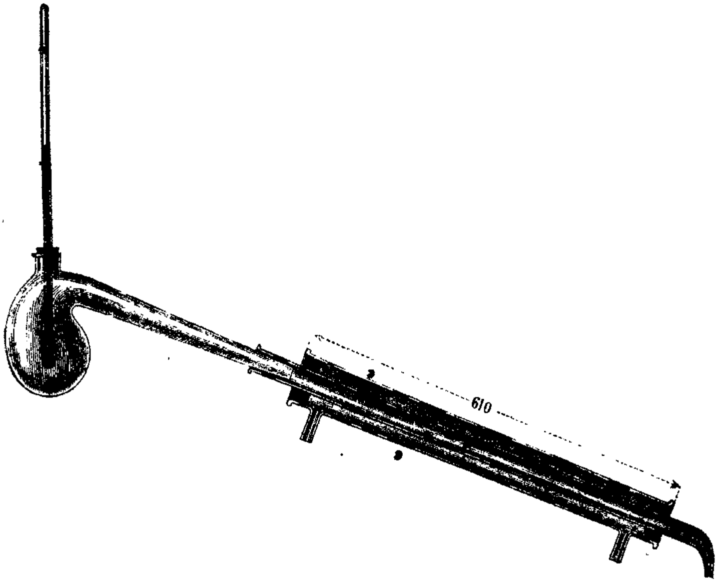

FIG. 207.

the tubulus by a cork so as to be vertical, and so that its bottom is $\frac{3}{8}$ in. distant from the bottom of the retort. The first marking or division of the thermometer is at 70°, which point should be well out of the retort, and the graduation should be continued up to 130°, with divisions at each $\frac{1}{2}$, or better $\frac{1}{5}$, of a degree Centigrade. Thermometers, otherwise similar, but differing some 6 in. in the height of the 100° mark give distinctly different percentages in benzol-testing.[1] The neck of the retort is inserted into the inner tube of a Liebig's condenser, and pushed as far as it will go. The condenser should be from 15 to 18 in. in length, and well supplied with cold water. The neck of the retort should not project too far into it, and, if necessary, should be cut short. No cork or other connection is necessary between the retort-neck and condenser-tube. Before use, both the retort and the condenser should be rinsed with a little of the sample and allowed to drain; or a little benzol is distilled in it and the residue carefully drained out. The graduated cylinder employed for measuring out the sample is next placed (without drying it) under the further end of the condenser-tube in such a manner as to catch all the distillate, while allowing it to drop freely. The retort is then heated by the naked flame of a Bunsen burner, furnished with an air-regulator working automatically with each movement of the tap, and surrounded by a cylinder to exclude currents of air.[1] The flame should be small, about the size and shape of a filbert, and, when the distillation of the benzol commences, must be so regulated that the condensed liquid shall fall rapidly in distinct drops, not in a trickle or a continuous stream.

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[1] Proper thermometers are obtainable from L. Casella, 147 Holborn Bars, London, E.C.

When the distillation commences, the flame is regulated, if necessary, and the rise of the thermometer carefully watched. The moment it registers 85°, the flame is extinguished. But as the thermometer even then still rises 0°·5 to 1°·0, this must be allowed for. A little experience shows the amount of this after-rise for each special case; thus, if it be 1°, the gas should be turned out when the thermometer registers 84°·5, because it will still rise to 85°·5, and thus 85°·0 may be considered the mean reading. Four or five minutes are allowed for the liquid in the condenser to drain into the measuring-cylinder, and then the volume of the distillate is carefully read off and recorded. The lamp is then relighted, and the distillation continued till the thermometer rises to 100° (observing the above-described precaution as to the after-rise), when the gas is turned off as before, and the volume of the distillate is read off, allowing time for drainage. The residual liquid in the retort is allowed to cool, and is then poured, to the last drop, into the measuring cylinder. A deficiency from the 100 c.c. originally taken will generally be observed. This deficiency, amounting to 1 c.c. or so, which is supposed to be caused by loss of benzol (although it is due far more to expulsion of acetylene and other gases), is added to the reading for each temperature, and the corrected volumes reported as the "strength" of the benzol examined. The variations in barometric pressure are allowed for by deducting or adding 1° C. for each inch below or above 30 in. Thus, if the barometer marks 29·5 in., the gas should be so extinguished that the thermometer may mark a mean temperature of 99°·5 instead of 100°. [According to my observations, this correction does not hold good for elevated situations, where the deviation of the barometer from 30 in. is too great; in that case the only practicable way is to distil pure benzene at the same time, and regulate the thermometer accordingly, as will be explained below. Altogether the method just described cannot be considered as accurate in any way.]

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[1] It is well to place the lamp in a deep tin basin to hold the benzol in the event of a retort cracking.

An anonymous writer (*Chem. News*, xliii., p. 93; li., p. 170) has asserted that for each $\frac{1}{10}$ in. lowering of the barometer 0·8 per cent. more is found than at the normal pressure; but this is evidently exaggerated. W. Thomson (*ibid.*, xliii., p. 115) recommends immersing the distilling-vessel entirely in a copper water-bath, so that the quantity passing over will be ascertained independently of the shape of the vessel, the state of the barometer, etc.; then the water might be siphoned off, and the copper box used as an air-bath for the higher temperatures. But it is here overlooked that the temperature inside the retort is several degrees below that of the water- or air-bath. In any case the water-bath would have to be brought, by the addition of common salt or the like, to such a temperature as to raise that inside the retort to 100°.

I have myself, in an extended investigation (*Chem. Ind.*, 1884, pp. 150 *et seq.*) in which I was aided by contributions from many of the largest producers and consumers of benzol, shown the great uncertainty attaching to all the ordinary testing methods founded on fractional distillation. It was found that the results were influenced by the following circumstances: the material of the retort (glass or metal); the shape of the same; the presence or absence of a dephlegmator; the exact position of the gas-delivery tube with reference to the level of the liquid, its width, and the way it was joined to the neck of the flask; the position of the thermometer; the length, width, and inclination of the condenser; the rate of distillation; the mode of reading-off; the barometric pressure. Uniform results can only be obtained by eliminating most or all of these disturbing influences, preferably in the following manner:—A quantity of the purest obtainable article is set aside as the "type." The sample to be tested is distilled in any suitable apparatus, the more rationally constructed the better, and immediately before or after a similar quantity of the "type" is distilled in the same apparatus exactly in the same way.

These investigations were continued by a special committee of the German Society of Chemical Industry, whose report has been made by Dr Bannow (*Chem. Ind.*, 1886, p. 328). There was an extraordinary diversity of opinion which ultimately led to the conclusion that different classes of substances, as alcohols, phenols, hydrocarbons, bases, etc., behaved differently with regard to their boiling-points, and that hence uniform rules for determining boiling-points can hardly be established. Bannow himself (the manager of Kahlbaum's works) employs for the most heterogeneous substances a globular retort of a capacity of 200 c.c. (say 7 oz.), made of platinum, silver, or copper, 0·7 mm. (=$\frac{1}{36}$ in.) thick, and 73 mm. (=about 3 in.) diameter, consisting of two flanged halves screwed together and made tight with a ring of wetted or oiled cardboard. [This arrangement has the drawback that the joint between the two half-globes is not always tight.] On the top there is a neck, 1 in. long and ¾ in. wide, provided with a glass still-head, ½ in. wide outside and 4 in. long, with a globular enlargement in the centre, and ⅜ above this a side-tube, branching off nearly at a right angle, sealed on without any contraction. The still rests on asbestos cardboard, with a circular hole of 1¼ in. diameter, and is heated by a plain Bunsen burner, whose flame always burns blue. The Liebig cooler is 800 mm. (=31 in.) long, and inclined at such an angle that the outlet is 4 in. below the inlet. The thermometer is made of thin glass, not thicker than half the width of the glass still-head; the mercury-bulb is placed in the centre of the globular enlargement. The thermometer-scale can be moved up and down by means of an adjusting-screw. The quantity of benzol placed in the retort is 110 c.c.; the 3 c.c. first distilling are rejected, and the distillation is carried on so that 5 c.c. per minute, or 2 drops per second, pass over. It is continued until the receiver has been filled up to 100 c.c. No correction is made for barometric pressure; but the thermometer-scale is adjusted by means of the screw before every test, by distilling 100 c.c. of a normal "type" and fixing the scale in the moment when 60 c.c. have passed over.—Most of these points were adopted by the other members of the Commission; but they all objected to the use of metal retorts, preferring glass, and to the rejection of the first and last portions of the distillate [which, in point of fact, is not possible in benzol-testing].

Mendelejeff (*J. Soc. Chem. Ind.*, 1883, p. 371) employed, for the testing of Caucasian petroleum, a special method, consisting in conducting the vapours issuing from the dephlegmator of the first retort through a tube which passes down to the bottom of the second retort, and from there through a dephlegmator of the same contrivance into a third, fourth, and fifth retort. When the temperature of the last retort has reached the height desired, the distillation is discontinued, and only resumed after the contents of the first retort have absorbed the contents of the remaining ones. Thus a very great number of fractions were obtained.

Forel (*Chem. Zeit.*, 1897, p. 393) employs a glass flask, A (Fig. 208), holding 200 c.c. The glass tube, B, 60 cm. long and 18 mm. bore, is connected by tube *a* with the Liebig cooler D, 80 cm. long. The thermometer C is divided from 0° to 100° in $\frac{1}{5}$°, and the mercury is entirely surrounded by the benzol vapour. One hundred c.c. are distilled off always in the same space of time (sixteen to seventeen minutes) and at the same barometric pressure of 738 mm. [how is that to be secured?]. At this pressure water boils at 99°·2; benzene boils with 734 mm. at 79·2, with 738 mm. at 79°·2, and with 743 mm. at 79°·4. For each 20 degrees of the thermometer not surrounded by vapour, 1° must be added.

The method now to be described, as published by F. Frank in *Chem. Ind.*, 1901, p. 240, and by Kraemer and Spilker, in Muspratt-Stohmann's *Chemie*, vol. viii., p. 34, has been worked out on the basis of the conditions laid down by me in 1884 (p. 863), and is an amplification of the prescription given by

Bannow (p. 964). It has been adopted by the leading German benzol manufacturers as the standard method.

1. The still, Figs. 209 and 210, is made of sheet copper, 0·6 to 0·7 mm. thick, of a globular shape, 66 mm. diameter, with a neck for receiving the thermometer tube 25 mm. long, 20 mm. wide at the bottom, and 22 mm. at the top.

2. The thermometer tube is of glass, 150 mm. long, 14 mm. wide inside, with a bulb 30 mm. wide, midway of its height. The side-tube, 8 mm. wide, is joined to it 10 mm. above the bulb, nearly at a right angle.

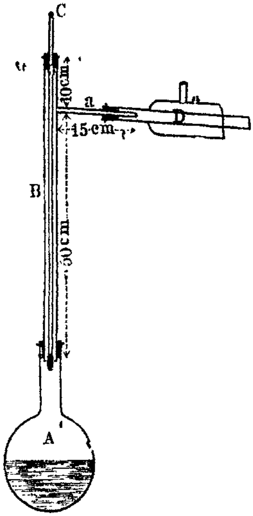

Fig. 208.

3. The still stands on an asbestos slab provided with a circular hole, 50 mm. diameter. The furnace has four round holes, 10 mm. below the top, for the escape of the products of combustion. The heating is performed by an ordinary Bunsen burner, 7 mm. wide, whose flame must be blue at any position of the tap.

4. The Liebig cooler is 800 mm. long, 18 mm. wide, and has such an inclination that the outlet of the inner tube is 100 mm. below the inlet.

5. The charge is 100 c.c. The distillation has to be carried

on in such manner that 5 c.c. pass over per minute—that

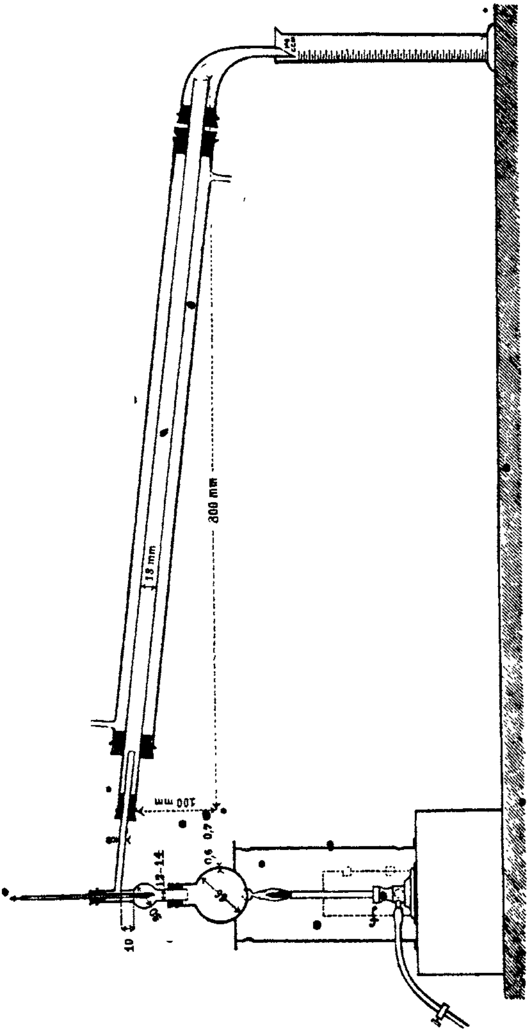

FIG. 209.

is, about two drops per second. It is carried on until the measuring cylinder is filled up to 95 c.c.

6. The thermometer should be made of thin glass. Its outside diameter should not be more than half the width of the tube. Its bulb should be placed in the centre of the bulb. For 90 per cent. and 50 per cent. benzol a thermometer is employed with divisions for each ½° C.; for pure benzene and toluene, it should be divided into 0°·1 C.

The thermometer is preferably provided with a scale, movable by means of a screw, which is set at 100° before every test by distilling 100 c.c. of distilled water at the moment when 50 c.c. have distilled over. Such a thermometer shows 80° as the boiling-point of pure benzene and 110° as that of pure toluene, whichever the barometric pressure may be, unless this has changed during these operations. Or else an ordinary thermometer is employed whose scale has been accurately compared with that of a standard thermometer, tested by the Reichsanstalt. In the latter case the boiling-point must be corrected for barometric pressure according to the rules given by Lenders (*Chem. Ind.*, 1889, p. 169) as follows:—(*a*) To the percentage of distillate, obtained at 100° C. at barometric pressures between 720 and 780 mm., in order to reduce this to 760 mm., add or deduct for each millimetre in the case of 50 per cent. benzol, 0·077; in the case of 90 per cent. benzol, 0·033. (*b*) When distilling between 720 and 780 mm., add or deduct to 100° C. for each millimetre in the case of 50

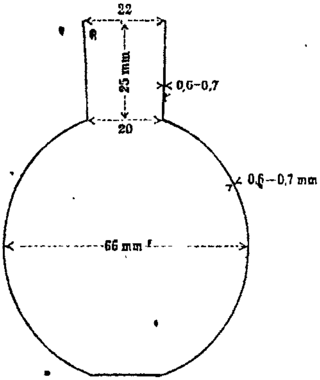

FIG. 210.

per cent. benzol, 0°·0461 C.; in the case of 90 per cent. benzol, 0°·0453 C., in order to obtain the real temperature corresponding to 760 mm. (*c*) For *pure* hydrocarbons the difference of temperature for each millimetre between 720 to 780 mm. is in the case of benzene, 0°·043; toluene, 0°·047; xylene, 0°·052 C.

An example will make this clearer. Suppose we have distilled a 90 per cent. benzol at a barometric pressure of 721·2 mm. (reduced to 0°) and obtained 88·8 per cent. distillate at 100°; 760 − 721·2 = 38·8; 38·8 × 0·033 = 1·28. Deducting this from 88·8, we obtain 87·5 as the real percentage of benzol.

When working according to these accurate and detailed descriptions, different chemists ought always to obtain the same results with the same material. If tested according to these prescriptions, commercial 90 per cent. benzol should yield *at least* 90 per cent. at 760 mm. pressure when distilled up to 100° C. Usually 90 to 93 per cent. distil over. Commercial 50 per cent. benzol should up to 100° yield at least 50 per cent., and up to 120° 90 per cent., but 53 and 93 per cent. are tolerated.

The designation "per cent." in all these cases does not mean that "90 per cent. benzol" contains 90 per cent. real benzene, C_6H_6, or "50 per cent. benzol" 50 per cent. C_6H_6, the remainder being toluene, xylene, etc. Very different mixtures fulfil the ordinary testing condition.

The requirements concerning the behaviour in distillation of the various descriptions of commercial benzol (*cf.* also p. 949 *et seq.*) may be stated as follows, the figures denoting the *minimum* required :—

Commercial 90 per cent. benzol .	90 p.c.	up to 100° C.		
„ 50 „ „ .	50	„ 100°,	90 p.c. up to	120°
„ benzol, No. III. .	0	„ 100°,	90 „	120°
„ „ IV. .	0	„ 120°,	90 „	145°
„ „ V. .	0	„ 130°,	90 „	160°
„ „ VI. .	0	„ 145°,	90 „	175°
„ heavy benzol . .	0	„ 160°,	90 „	190°

Pure benzol should yield		95 per cent. within 0°·8
„ toluol	„	95 „ „ 0°·8
„ xylol	„	0 up to 136°, 90 per cent. up to 140°
Cumole	„	0 „ 163°, 90 „ „ 172°
Pseudocumol	„	0 „ 167°, 90 „ „ 170°

Benzol free from thiophen has the same boiling-points as pure benzol.

In order to avoid the influence of *carbon disulphide* on the testing of benzol, which frequently leads to awkward irregularities (*cf.* the statements of Watson Smith, p. 937), Nickels (*Chem. News*, xliii., pp. 148 and 250) treats the benzol twice with 10 per cent. by volume of a hot saturated solution of caustic potash in absolute alcohol, agitates for two hours, filters from the precipitate of potassium xanthate (*cf.* about this, *infra*, p. 982), removes the alcohol from the filtrate by twice washing with its own volume of water, removes the water suspended and dissolved by agitating with a little plaster of Paris, and distils as usual. Thus much more constant results are obtained than without that purification; the benzol now shows a lower sp. gr. (0·882 or 0·880, instead of 0·885), and is quite free from alliaceous smell.

The following results were obtained by Nickels from the same benzol:—A, when distilled in an 8-oz. retort in the ordinary way; B, after removing the carbon disulphide in the manner described above; C, when the *purified* benzol was distilled in a three-bulb apparatus instead of in an 8-oz. retort:—

	A. Commercial 90 per cent. benzol in 8-oz. retort.	B. A after being purified from CS_2 in 8-oz. retort.	C. B distilled in a flask with three-bulb apparatus.
Spec. grav. at 15°·5 .	0·884	0·881	0·881
First drop distilled at .	79°·5	83°·4	...
5 per cent. " .	...	84°·2	81°·25
10 " " .	...	84°·3	82°·0
20 " " .	...	85°·0	82°·8
25 " " .	84°·0	...	...
30 " " .	85°·0	85°·8	83°·0
40 " " .	85°·4	86°·4	83°·5
50 " " .	86°·4	87°·1	84°·7
60 " " .	88°·0	88°·3	85°·3
70 " " .	90°·0	90°·0	86°·5
80 " " .	93°·0	93°·0	89°·3
90 " " .	100°·0	100°·0	100°·0
95 " " .	...	112°·4	111°·8

By operating on 300 c.c. of the same sample, removing the carbon disulphide by alcoholic potash, and several times repeating the process of fractionating with the three-bulb apparatus, Mr Nickels obtained the following results as indicative of the proximate analysis of the benzol tested:—

	Per cent.
Carbon disulphide	1·5
Light hydrocarbons, sp. gr. 0·872 (not nitrifiable, probably chiefly amylene and acetonitrile) . .	3·5
Benzene, sp. gr. 0·885, distilling within a range of 2° .	78·4
Toluene, sp. gr. 0·8715, distilling within 2° . .	16·6
	100·0

It is very desirable that the present empirical and conventional mode of benzol-testing should be replaced, at any rate in important cases, by the above treatment, based on scientific principles.

Determination of Toluene.—H. G. Colman (*J. Gas Lighting*, 1915, cxxix., pp. 196 and 314) gives special rules for the determination of toluene in commercial toluol and solvent-naphtha. The sample of toluol is distilled from a standard Engler flask under the prescribed conditions, and the volumes of the fractions collected below 105°, from 105° to 117°, and above 117°, are noted by the aid of a table which is based on a large number of distillations of mixtures of benzene, toluene, and xylene; the percentage of toluene may be derived from the volumes of the extreme fractions. The table is only applicable to mixtures which contain 50 to 75 per cent. of toluene. Other samples must be diluted with benzene, toluene, or xylene, so that the extreme fractions are, each of them, not less than 5 per cent. nor more than 50 per cent. of the total distillate. If the sample contains paraffins, 100 c.c. may be fractionated by a Young twelve-bulb column, and the percentage of the toluene fraction, 107° to 115°, corrected by measuring its density. For every 0·001 that the density is below 8·868, a reduction of 0·75 per cent. is made. In the case of commercial solvent-naphtha, the sample is distilled at the rate of one drop per second, with an efficient fractionating column, to give at least 35 c.c. of distillate below 138°. If 200 c.c. of the sample fail to yield 35 per cent. of this fraction, it may be considered to be practically free from toluene.

Otherwise, 35 c.c. of the distillate are mixed with 57 c.c. of toluene and 15 c.c. of benzene, and examined as above.

2. *Specific Gravity.*

The specific gravity is usually only ascertained by the hydrometer, but for accurate purposes a Mohr's balance should be used. The average specific gravities of commercial benzols are stated by F. Frank (*Chem. Ind.*, 1901, p. 262) as follows:—

Pure benzene	from	0·883	to	0·885
Benzene free from thiophen	„	0·883	„	0·884
Toluene	„	0·870	„	0·871
Xylene	„	0·867	„	0·869
Benzol, 90 per cent.	„	0·880	„	0·883
„ 50 „	„	0·875	„	0·873
„ 0 „	„	0·870	„	0·872
Solvent-naphtha boiling up to 160°	„	0·874	„	0·880
„ „ 175°	„	0·890	„	0·910
"Heavy benzol"	„	0·920	„	0·945

A lower specific gravity than the limit here given points to the presence of paraffins in more than usual quantity, a higher one in the case of Nos. I. and II., especially to carbon disulphide, in Nos. III. to VI. to insufficient washing.

Haissig's attempt (*Chem. Zeit.*, 1897, p. 939) to draw conclusions on the composition of benzols from their specific gravities is proved to be untenable by a look at the above-given table, and has been expressly repudiated by Spilker and Bindewald (*ibid.*, 1898, p. 27).

3. *Tests for Paraffins (admixture of Shale Oil, etc.).*

Sulphonation Method.—We first quote this test for paraffin, described by F. Frank and by Kraemer and Spilker (Muspratt's *Chemie*, 4th ed., viii., p. 43) as the most reliable:—Shake 200 g. of the sample in a separating-funnel with 500 g. of fuming sulphuric acid, containing 20 per cent. SO_3, during a quarter of an hour, avoiding a rise of temperature, and allow two hours for settling. Run off the acid and repeat the treatment with a fresh quantity of acid twice over, settling and drawing off the acid as before. When 1500 g. of that acid have been used, all the hydrocarbons, except the paraffins, are usually dissolved.

Collect the oil by itself, and let the acid run in a slow stream on to its own weight of crushed ice, placed in a 3-litre flask, with frequent shaking, so that the temperature does not rise over 40°. Then distil over a free flame directly into a separating-funnel, holding 100 c.c. When, apart from the first distilling oil, 50 c.c. of water has passed over, you may count upon having recovered any paraffin, dissolved or mechanically mixed with the sulphonic acids. Draw off the water, unite the paraffin with the oil previously collected, and shake repeatedly, every time with 30 g. of the fuming sulphuric acid, until no further diminution of volumes takes place. Wash with a small quantity of distilled water, and weigh the oil, which represents the paraffins contained in 200 g. of the benzol.

The word "paraffin" in this description denotes all substances which cannot be sulphonated or destroyed by fuming sulphuric acid. That means that any naphthenes present, as well as carbon disulphide, are included among the paraffins. Since practically the designation "paraffin" is identified with "non-nitrifiable," the figures obtained as above are applicable to this (a direct estimation of the nitrifiable constituents will be described *infra*). If the carbon disulphide has to be distinctly deducted, it must be estimated by one of the processes described *infra* in No. 4.

Benzols Nos. I. to III., as well as toluol, generally yield only a few tenths, up to at most 1 per cent. of paraffin. If more than this is found, it points to an adulteration with shale oil, petroleum, or the like.

To distinguish coal-tar benzol or naphtha from petroleum- or shale-spirit, etc., which are also frequently called "benzoline, naphtha," etc., and which may easily occur as adulterations of the former, is not difficult. Both products can be at once distinguished by their smell, if unmixed; but in mixtures the smell of coal-naphtha prevails over even a very large addition of petroleum or shale-spirit. The specific gravity affords a good test (p. 972): with coal-naphtha it is always above 0·867 at 15°, with petroleum spirit, etc., below or at most very little above 0·700. There is, however, the drawback that carbon disulphide *raises* the density of benzol, so that it would compensate a lowering produced by petroleum hydrocarbons. A direct estimation of the paraffin, as described above, gives an indication for the presence of shale oil, petroleum, and the like. Very distinct is the reaction with nitric acid, which at once acts upon the aromatic hydrocarbons of coal-tar, but hardly at all upon the fatty compounds of petroleum or paraffin oil.

The following useful synopsis of the characters of the two kinds of products has been made by A. Allen (*Chem. News*, xl., p. 101):—

Petroleum spirit, Benzoline, Benzine.	*Coal-tar Naphtha, or "Benzol."*
1. Consists of heptane (C_7H_{16}) and its homologues.	1. Consists of benzene (C_6H_6) and its homologues.
2. Heptane contains 84·0 per cent. of carbon.	2. Benzene contains 92·3 per cent. of carbon.
3. Commences to boil at 54° to 60° C.	3. Commences to boil about 80° C.
4. Specific gravity at 15°·5 about 0·69 to 0·72.	4. Specific gravity about 0·880.
5. Smells of petroleum.	5. Smells of coal-tar.
6. Dissolves iodine, forming a solution of a raspberry-red colour.	6. Dissolves iodine, forming a purple-red liquid of the tint of an aqueous solution of potassium permanganate.
7. Does not sensibly dissolve coal-tar pitch, and is scarcely coloured by it even on prolonged contact.	7. Readily dissolves coal-tar pitch, forming a deep-brown solution.
8. When shaken cold with one-third of its volume of fused crystals of absolute carbolic acid, the latter remains undissolved and forms a separate lower stratum.	8. Miscible with absolute carbolic acid in all proportions.
9. Requires two volumes of absolute alcohol, or 4 or 5 volumes of methylated spirit of sp. gr. 0·828, for complete solution at the ordinary temperature.	9. Miscible with absolute alcohol in all proportions. Forms a homogeneous liquid with an equal measure of methylated spirit of sp. gr. 0·828.
10. Warmed with four measures of nitric acid of sp. gr. 1·45, the acid is coloured brown, but the spirit is little acted on and forms an upper layer.	10. Completely miscible with four measures of nitric acid of sp. gr. 1·45, with great rise of temperature and production of dark-brown colour. A portion of the nitrobenzene produced may separate out as the liquid cools.

No. 10 is capable of giving quantitative results in separating the two kinds of oil. The oil to be tested is treated with nitric acid of sp. gr. 1·45 in a small flask with an inverted condenser. When the action has nearly ceased, the whole is poured into a narrow graduated tube; the measure of the upper layer indicates approximately the amount of petroleum spirit present. If the proportion of benzene is considerable, the nitrobenzene formed may not remain completely dissolved in the acid, but form a layer of dark-brown colour below the stratum of petroleum spirit. Nitrobenzene and petroleum spirit are readily miscible in the absence of nitric acid; but agitation with strong nitric acid dissolves out the nitrobenzene, a portion of which may rise and form an intermediate layer, as above described. According to Lainer (*Chem. Rev.*, 1897, p. 55), benzol, when shaken up with a trace of alcohol (not below 95 per cent.), gets muddy, whilst benzin remains clear.

Gawalowski (*Chem. Zentr.*, 1897, i., p. 1038) recommends as a reagent picric acid, which is easily soluble in coal-tar benzol, but almost insoluble in petroleum spirit. If the latter is added to an equal volume of a concentrated solution of picric acid in benzol, the acid is precipitated in the form of crystals.

Holde (*Fischer's Jahresber.*, 1895, p. 554) employs tar-pitch previously exhausted with boiling petroleum spirit. A gram or so of this pitch is placed on a small filter, and 5 c.c. of the liquid poured over it. From 5 to 10 per cent. tar-benzol dissolved in petroleum spirit is recognized by the yellow colour of the solution, and an approximate colorimetric estimation can be thus performed.

For recognizing and estimating coal-tar benzol, etc., in the presence of rosin oil and mineral oils, Valenta (*Chem. Zeit.*, 1906, 266) shakes the mixture in a graduated cylinder with a solution of dimethyl-sulphate, which dissolves the benzol hydrocarbons easily, the rosin oil in the cold only with difficulty, and the mineral oils not at all.

Dimethyl-sulphate is also employed by Graefe (*Laboratoriumsbuch für die Braunkohlenteerindustrie*, p. 134), according to whom lignite oils are very little soluble in this reagent, by shaking out mixtures of coal-tar oils with heavy petroleum oils with one and a half times their quantity of dimethyl-sulphate. The diminution of volume indicates directly the quantity of coal-tar oils, but when treating in the same way mixtures of coal-tar oils with lignite oils, the proportion of the latter is found too high by 10 per cent.

Boehme (*Chem. Zeit.*, 1906, p. 633) discusses the estimation of benzol, petroleum, and distillates from this in oil of turpentine.

The *nitrating test*, to be described now, was formerly very generally employed to find the real benzol, as distinct from the "paraffin." It is burdened by some errors, but we shall describe it here, since it is still a good deal in use, as giving an idea of how much nitrobenzene may be expected on the large scale:—Place 100 c.c. benzene in a flask of about 500 c.c. capacity, provided with a dropping-funnel, *a*, and a long tube, *b*

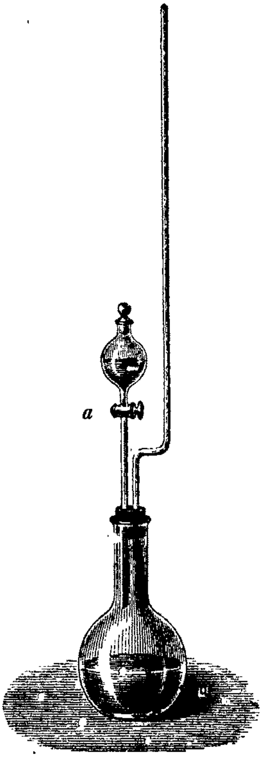

FIG. 211.

(Fig. 211), for condensing any hydrocarbon volatilizing. Prepare also a mixture of 150 g. nitric acid of sp. gr. 1·4, and 180 or 200 g. sulphuric acid, sp. gr. 1·84; which must be allowed to cool before use. Run this, drop by drop, through the tap-funnel *a* into the benzol, shaking this up almost constantly. As soon as the temperature rises, cool the flask by immersing it in a dish full of water. When all the acid has been added, and when no further rise of temperature takes place spontaneously, heat the flask gently for an hour or two (during this time the tube *b* is best replaced by a proper reflux-condenser). Allow the whole to settle, and separate the lower acid layer by means of a separating-funnel from the crude nitrobenzene. Dilute the acid with several times its bulk of water; any oily liquid separating after a few hours' rest is added to the nitrobenzene. Wash the crude nitrobenzene three times with its own bulk of water, once with a very dilute solution of caustic soda (if a concentrated solution is employed, an emulsion is formed which is very awkward to manage), and again with water, taking care that no oil is lost in separating the washings. The well-settled liquor can be at once tested for its specific gravity, which, in the case of 90 per cent. benzol, ought to be 1·20; with 50 per cent. benzol, 1·19 at 15°; but this is not decisive, as the nitrobenzol is not quite free from water, and some benzol may have escaped nitrification. The liquor is therefore distilled from a fractionating-flask (Fig. 213, p. 990) till the temperature has reached 150°, and the distillate is once more nitrated, but this time with large excess of the acid mixture; anything remaining undissolved may be regarded as non-nitrifiable hydrocarbons. Theoretically, 100 parts of benzene furnish 157·6 of nitrobenzene; 100 parts of toluene, 148·9 of nitrotoluene.

4. *Titration with Bromine.*

The object of this is to ascertain how far the purifying operations have removed from the crude benzol the substances which add bromine and are resinified in practical use. The test is, therefore, applied only to *washed* benzol and toluol; it is not applicable to xylol and those commercial benzols which contain a considerable quantity of it, since the higher homologues of benzene even in the pure state are not indifferent to bromine. Häussermann (*Chem. Zeit.*, 1887, p. 303) certainly contends that ordinary purified benzol, Nos. I. and II., gives no reaction with bromine, although it may contain useless hydrocarbons (paraffins), but the object of the test is to indicate just those hydrocarbons which add bromine.

The following prescriptions for this test are given by

F. Frank and by Kraemer and Spilker. The test liquor is a decinormal solution of potassium bromide-bromate, prepared by dissolving 9·9167 g. potassium bromide + 2·7835 potassium bromate in a litre of water, and giving out 0·008 g. bromine per cubic centimetre on the addition of dilute sulphuric acid. Put 5 c.c. of the sample into a stoppered jar holding about 50 c.c., add 10 c.c. of dilute (20 per cent.) sulphuric acid, and quickly add as much of the bromine test liquor as the sample takes up after shaking it up uninterruptedly for five minutes. The end of the reaction is indicated when the oil, floating on the top, after five minutes' standing,[1] shows an orange-red colour, and when a drop of it, put on freshly prepared zinc-iodide starch paper, *momentarily* produces a dark blue colour. The number of cubic centimetres of the bromine solution used is stated as such. It is best to make a preliminary test before the proper one. "Pure" benzene and toluene should give a distinct reaction after adding less than 0·4 c.c. of the bromine solution to 100 c.c. of the sample; commercial 50 per cent. and 90 per cent. benzols on the average require 0·6, rarely over 1 g. bromine, but commercial xylol discolours after two minutes about 2 g. bromine, and much more after standing for some time. Since the reaction is promoted by the action of light, any *bright* light must be avoided during the test.

5. *Testing with Concentrated Sulphuric Acid.*

This test, proposed by J. K. Smith (*Chem. Zeit.*, 1899, p. 224), has also the object of ascertaining whether the purification of benzol on the large scale by washing it with sulphuric acid has been carried out to a sufficient extent, and whether any resinifiable substances, like cumarone, indene, etc., have been removed as much as possible.

On being mixed with a large quantity of strong sulphuric acid, say, 20 : 1, *pure* benzene and toluene are hardly coloured at all; other benzols take a yellow colour which should be as slight as possible. The observations of different analysts as to this colour cannot be directly compared by general expressions, wherefore F. Frank and Kraemer and Spilker give the following exact prescriptions for testing 90 per cent. and 50 per cent. benzol, pure benzene, toluene, and xylene.

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[1] The original prescription was: to leave the sample standing for *fifteen* minutes. Spilker afterwards found that this was too much, and that *five* minutes should not be exceeded in the case of benzol, and *half a minute* in that of toluol.

Shake 5 c.c. concentrated sulphuric acid with 5 c.c. of the sample in a 15 c.c. stoppered bottle vigorously for five minutes, allow to stand one or two minutes, and then compare with a solution of potassium bichromate in pure 50 per cent. sulphuric acid, contained in a small stoppered bottle, exactly like the first, holding 5 c.c. of that solution + 5 c.c. purest benzene. When thus compared, 50 per cent. and 90 per cent. benzol should exhibit a colour like that of a solution of 0·5 to at most 1·5 g. chemically pure potassium bichromate in 1 litre of 50 per cent. sulphuric acid. Xylol will produce a colour like a solution of 1·2 to 2·0 bichromate per litre; with "pure" benzene and toluene the sulphuric acid should give no colour at all. The colour of the bichromate solution used as type keeps for a long time, but the pure benzene, used for the top layer, should be renewed every time.

The German Inland Revenue Office has adopted this method for testing the benzol No. I. (90 per cent.), used for denaturing spirits of wine. The higher benzols, Nos. II. to VI., may also be examined in this manner, but they may yield very different results according to the use for which they are intended.

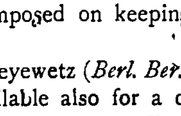
This test is also employed at some aniline-colour works for ascertaining the *loss of technical benzols by the purification process with sulphuric acid.* One thousand g. of the benzol or toluol are shaken up in a large tap-funnel with 125 g. sulphuric acid of sp. gr. 1·84 for half an hour, and then allowed to rest. When the two liquids in the funnel have separated, the acid is carefully run out; the benzol remaining in the funnel is several times washed with 200 c.c. water each time, and at last with weak caustic-soda solution (say 5° Bé.). Usually this purification is sufficient, but in the case of very bad benzols it must be repeated once or even twice, employing now only 50 c.c. sulphuric acid. Whether this is necessary or not, is learned by the just described reaction with bromine; the benzol used for this is always put back to the principal portion. The washed benzol is now dried by means of a few pieces of fused calcium chloride, and weighed. The difference between the 1000 g. employed and the weight now found indicates the loss by purification.

6. *Testing for the Smell.*

The smell of thoroughly washed benzols is mild and pleasantly aromatic, whereas unpurified or imperfectly washed benzol has a sharp, disagreeable, or even empyreumatic smell. It is observed by pouring a few drops on to pure filtering paper, and leaving it to evaporate in the air.

7. *Examination for Carbon Disulphide.*

(a) *Qualitative.*—Liebermann and Seyewetz (*Ber.*, 1891, p. 788) have indicated the following reaction for discovering the presence of CS_2 in benzol, based on a previous observation of E. Fischer's. They agitate 10 c.c. of the benzol with 4 or 5 drops of phenylhydrazine several times during one to one and a half hours. If as much as 0·2 per cent. CS_2 be present, a thick, white, crystallized precipitate is formed, converting the whole liquid into a magma. In the presence of 0·03 per cent. CS_2 the precipitate is still quite plainly visible; at 0·02 per cent. (0·17 g. per litre), the limit of the reaction is reached, and it is best to promote the crystallization by throwing in a tiny crystal of the compound formed. This is the phenylhydrazine-phenylsulfocarbazinate, discovered by E. Fischer:



$$CS\begin{cases} S\,.\,N_2H_2\,.\,C_6H_5 \\ N_2H_4\,.\,C_6H_5 \end{cases}$$

Fusing-point 97° C., insoluble in benzene, easily soluble in acetone, precipitated from that solution in orange-coloured flakes. It is very quickly decomposed on keeping, or by contact with water.

Liebermann and Seyewetz (*Berl. Ber.*, 1891, p. 788) mention that reaction as available also for a quantitative estimation of CS_2 in benzols. According to Frank (*Chem. Ind.*, 1901, p. 262), this method, although very accurate, has not found entrance in the works' laboratories, as being too lengthy and troublesome. *Cf.* also *infra*, p. 983, the process described by Bay.

The presence of CS_2 can be also detected by alcoholic potash, which forms crystals of potassium xanthate (see below), or by alcoholic ammonia, which forms ammonium sulphocyanide, easily recognizable by the blood-red reaction with ferric chloride. J. B. Cohen (*Chem. News*, 1886, p. 3016) has tried to apply Traube's capillarometer (devised for estimating fusel oil in spirit of wine) for discovering carbon disulphide, as well as fatty hydrocarbons, in benzol. His own paper shows that this reaction can hardly as yet lay claim to more than a qualitative value.

(b) *Quantitative Estimation.*—Holland and Phillips (*J. Soc. Chem. Ind.*, 1884, p. 296) put 2 c.c. of the benzol to be tested into a piece of combustion-tubing about 12 or 13 in. long, sealed at one end and drawn out at the other extremity, so as to form a funnel; they add 5 c.c. of a solution of ferric chloride, containing 240 g. $FeCl_3$ in 1000 c.c., and 10 c.c. of strong ammonia. The tube is carefully sealed before a lamp and well shaken; it is then wrapped in a cloth and immersed in boiling water for an hour or so. At the expiration of that time the tube is taken out, allowed to cool, and opened. The following reaction will have taken place in the first instance:—

$$CS_2 + 4NH_5O = NH_4 . CNS + (NH_4)_2S + 4H_2O,$$

but the presence of ferric chloride will have caused the sulphur of the ammonium sulphide to be converted into FeS. This is now oxidized along with the sulphur of the thiocyanate in the following manner:—The contents of the tube are transferred to a flask holding about ½ litre and are evaporated, just to dryness, by careful manipulation over a Bunsen flame: 20 c.c. of fuming nitric acid is added, and the whole is boiled nearly to dryness. If any sulphur is left unoxidized, a little more nitric acid must be added. Lastly, hydrochloric acid is added and some water, the solution is filtered, and the sulphuric acid in the filtrate is determined in the usual manner as barium sulphate. As it is not possible to get the whole of the ferrous sulphide out of the tube with water alone, this is best done by means of a little hydrochloric acid and a few grains of potassium chlorate. This method is probably not much employed in factories, no more than the titrimetric method of Goldberg (*Z. angew. Chem.*, 1899, p. 75).

The method usually employed for estimating the carbon disulphide in benzol is its conversion into *xanthogenate*, by shaking it with an alcoholic solution of potash, as first indicated by A. W. Hofmann (*Berl. Ber.*, 1880, p. 1732). Several chemists have worked out methods based on this reaction (*e.g.* Nickels, *Chem. News*, xliii., p. 148; Biehringer, *J. Gasbeleucht.*, 1890, p. 341; Schmitz-Dumont, *Chem. Zeit.*, 1897, pp. 487 and 510). The reaction taking place is this:

$$CS_2 + KOH + C_2H_6O = H_2O + CS(O.C_2H_5)SK.$$

The potassium xanthogenate formed is transformed into insoluble cupric xanthogenate by addition of cupric sulphate, which can be carried out either by volumetric or by gravimetric methods.

The following is a prescription for carrying out the xanthogenate test, as generally used in Germany (Frank, *loc. cit.;* Kraemer and Spilker). Mix 50 g. benzol with 50 g. alcoholic potash solution (prepared by dissolving 11 g. caustic potash in 90 g. absolute alcohol), and let the mixture stand at the ordinary temperature for some hours. Add about 100 c.c. water, shake well up, separate the aqueous liquor from the benzol, and wash this several times with water. Unite all the aqueous liquids, and estimate the potassium xanthogenate formed from the CS_2 by the reaction:

$$CS_2 + KOH + C_2H_6O = H_2O + CS(O.C_2H_5)SK,$$

by titrating it with a copper solution containing per litre 12·475 g. crystallized cupric sulphate, and indicating per cubic centimetre 0·0076 g. CS_2. For this purpose neutralize the solution with acetic acid, and add the copper solution until a drop, taken out with a glass rod and placed on a piece of filter-paper beside a drop of a solution of potassium ferrocyanide, produces a red colour at the point of contact. The final point is also approximately indicated by the fact that the precipitated cupric xanthogenate, which is at first in the shape of fine powder, aggregates in the shape of lumps. The quantity of potash indicated above is sufficient up to a percentage of 5 per cent. CS_2 in the benzol. This will be enough in most cases, since even the richer benzols rarely contain upwards of 1 per cent. CS_2, and the poor ones none at all.

Edward S. Johnson (*J. Amer. Chem. Soc.*, xxviii., p. 1209; *Chem. Zentr.*, 1906, ii., p. 1283) maintains that the composition of the cuprous xanthogenate is not constant, and the sulphur is then found too low, on an average by 10 per cent. He assumes the proportion of CS_2 to the xanthogenate to be on the average = 1 : 1·750. The composition of the precipitate is influenced by its quantity and by the time it remains in contact with the mother-liquor. The *total sulphur* is found by evaporating the sample in a current of hydrogen and burning the vapours in an atmosphere of oxygen, whereupon the sulphur is estimated in the ordinary way.

Bay (*Comptes rend.*, cxlvi., p. 132) employs the reaction of Liebermann and Seyewetz (*supra*, p. 980), in the precipitation of CS_2 with phenylhydrazine, quantitatively. The compound formed is $CS_2(C_6H_5 . NH . NH_3)_2$, white, crystalline, very unstable in solution, and slightly so in the dry state, but it will keep long enough if a determination is effected in the course of a day. The precipitation is complete in two or three hours. Double, tared filters are used, the excess of phenylhydrazine is carefully washed out with pure benzene, and the precipitate is dried in a vacuum. The results are a little high, owing to the difficulty of washing the precipitate completely.

Stavorinus (*J. Gasbeleucht.*, xlix., p. 8; *Chem. Zentr.*, 1906, i., p. 705) employs the method of Petersen (*Z. anal. Chem.*, xlii., p. 406) for estimating the carbon disulphide in benzol. Mix 25 c.c. benzol with 70 c.c. alcohol (96 per cent.) in a beaker, add 10 c.c. caustic-potash solution (8 per cent.), allow to stand for half an hour, then add 5 c.c. concentrated, acid-free hydrogen peroxide ("*Perhydrol Merck*"), evaporate the alcohol on the water-bath, add 200 c.c. water, acidify with hydrochloric acid, and precipitate the sulphuric acid produced from the xanthogenate formed in the first instance by the oxidizing action of the hydrogen peroxide as barium sulphate. One g. $BaSO_4$ = 0·16303 g. CS_2. *Thiophen* is not acted upon by the alkaline peroxide solution. This reaction can also be carried out as a volumetric method, in this way: mix 25 c.c. benzol with 70 c.c. alcohol, add 10 c.c. normal potassium-hydroxide solution; after half an hour add 5 c.c. perhydrol, evaporate the alcohol, dilute with

100 c.c. water, and titrate back with fifth-normal sulphuric acid (using methyl-orange as indicator). Every cubic centimetre normal alkali consumed is = 19 mg. CS_2.

Ellerton (*J. Gas Lighting*, 1912, cxvii., p. 222) gives the following rule for finding the *approximate* contents of carbon disulphide in benzol. Deduct from the specific gravity found (say, 0·9000) the figure 0·885, and divide the remainder by 0·00346, thus:

$$\frac{0.900 - 0.885}{0.00346} = 4.3 \text{ per cent.}$$

8. *Testing for Thiophens.*

The reactions proving the presence of thiophen in benzol were partly known before its discovery, but erroneously ascribed to benzene itself. The following are the most important of these reactions.

Laubenheimer's *indophenine reaction* is carried out as follows:—In a small porcelain dish, previously rinsed with pure sulphuric acid, place a grain of isatine, into this a few cubic centimetres pure concentrated sulphuric acid, and into this the benzol to be tested. Put a watch-glass on and leave standing. If any thiophen be present, blue rings will appear in the benzol, the following reaction taking place:—

$$\underset{\text{Isatin.}}{C_8H_5NO_2} + \underset{\text{Thiophen.}}{C_4H_4S} = \underset{\text{Indophenin.}}{C_{12}H_7NOS} + H_2O$$

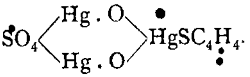
Thus as little as 0·01 per cent. thiophen may be discovered. *Cf.* V. Meyer (*Ber.*, 1882, p. 2893); Bauer (*ibid.*, 1904, p. 1244); Storch (*ibid.*, 1904, p. 1961); Liebermann and Peus (*ibid.*, 1904, p. 2461). Thiotolen produces a blue colour with a shade of red, thioxen a purple colour.

Liebermann's reagent for thiophen (*Ber.*, 1887, p. 3231) is *nitroso-sulphuric acid*, produced by adding to pure concentrated sulphuric acid 8 per cent. potassium nitrite and allowing the mixture to stand in an open vessel until 7 or 8 per cent. moisture has been attracted from the air, and a large portion of the potassium hydrosulphate has crystallized out; or else by dissolving amyl nitrite in sulphuric acid. In order to test benzol for thiophen, 2 or 3 drops of the reagent are put in a test-tube, 1 c.c. of benzol is added and the mixture shaken up. The acid, spreading out on the sides of the tube, at first shows a red colour, but this in the presence of thiophen soon turns into green, and finally into a splendid blue colour, by the formation of the compound: $C_8H_5NS_2O_2$. If much thiophen is present, the colour appears at once; if only 2 or 3 per cent. is present, it comes out in a few minutes, and with very slight quantities only after a quarter of an hour. This reaction fails when very minute quantities of thiophen are present, *e.g.*, in the case of some coke-oven benzols, as pointed out by Schwalbe (*Ber.*, 1904, p. 324), but Liebermann and Peus (*loc. cit.*) even in such cases got it after three hours, especially by improving it in this way: pouring off the benzol and adding to the acid at the bottom a great excess of sulphuric acid. Thus 0·1 per cent. thiophen can be found.

Kreis (*Chem. Zeit.*, 1902, p. 523) proves the presence of thiophen in benzol by the (soon evanescing) coloration produced by thallin. This reaction may be also applied for testing for thiotoluene in toluene, but it fails with thioxenes.

Quantitative Estimation.—Denigès (*Comptes rend.*, cxx., pp. 628 and 781) estimates the thiophens as follows:—In a stoppered 60 c.c. bottle 20 c.c. *mercurial solution* (prepared by dissolving 50 g. HgO in 200 c.c. concentrated sulphuric acid and diluting to a litre) is shaken with 2 c.c. benzol and heated, with agitation, on a boiling water-bath for an hour. After cooling, the precipitate is collected on a weighed filter, washed with hot water, and dried at 110° or 115°. Its weight multiplied by 0·0758 represents the thiophen.

The process of Denigès can be carried out volumetrically as follows (*Bull. Soc. Chim.* [3], xv., p. 1064):—Mix 2 c.c. benzol with 30 c.c. methyl alcohol, free from acetone, and quickly add 10 c.c. of a solution of 50 g. red mercuric oxide in 200 c.c. sulphuric acid and 1000 water. Shake well, and after twenty-four hours filter off the compound formed



Put 21 c.c. of the filtrate, corresponding to 1 c.c. benzol, in a litre flask, and add 350 c.c. water, 15 c.c. liquor ammoniæ, 10 c.c. of a solution of potassium cyanide equivalent to a decinormal solution of argentic nitrate, and 5 or 6 drops of a 20 per cent. solution of potassium iodide. Clear up the solution in case of need by heating, and add decinormal argentic nitrate solution up to the formation of a permanent cloud. If n be the number of cubic centimetres of the silver solution used, the quantity of thiophen contained in 1 litre of the benzol is $=(n-0{\cdot}3 \text{ c.c.}) \times 2{\cdot}8$ g.

Dimroth (*Ber.*, 1902, p. 2035) found that at 100° C. thiophen is acted upon by a solution of *mercurous acetate*, while benzol remains unchanged. He proposes this reaction as a basis for the estimation of thiophen in benzol. Paolini and Silbermann (*J. Chem. Soc.*, 1915, cviii., ii., p. 806) employ the same method.

Schwalbe (*Chem. Zentr.*, 1905, ii., pp. 335 and 1126) declares the methods of Denigès and Dimroth not to be accurate. He employs the indophenin reaction (*vide* p. 984) to quantitative colorimetric estimations, by which he states that he can estimate 0·05 per cent. thiophen in a stoppered shaking-cylinder, and down to 0·01 in an open dish. Intervals of 0·02 per cent. thiophen can be well recognized. The lower limit of the method is at 0·05 per cent., the upper limit at 0·5 per cent. thiophen—that is the limits between which the thiophen percentage of commercial benzol varies. For carrying out this method, a number of test solutions must be prepared from benzol free from thiophen and absolutely pure thiophen (the brand sold by Kahlbaum is perfectly pure), viz., solutions containing 0·5, 0·25, 0·1, 0·075, 0·05, 0·025, and 0·01 per cent. thiophen; besides, a solution of 0·5 g. isatine in 1000 g. pure sulphuric acid, which keeps for several months. Twice 25 c.c. isatine-sulphuric acid is put in a 100 c.c. stoppered flask each. To each of these 25 c.c. pure concentrated sulphuric acid is added, and to one of them is added 1 c.c. of the benzene-thiophen test solution, to the other 1 c.c. of the benzol to be tested. The flask is closed by its stopper, vigorously shaken during five minutes, allowed to settle, and placed on a white surface, in order to observe the coloration produced. The colour, if the percentage of thiophen is not below 0·05 per cent., is under all circumstances to begin with olive or bluish green. The less thiophen is present the more slowly the coloration sets in, and is all the more verging towards green. Fifteen minutes suffice for establishing the result. If a commercial benzol has to be examined, you must commence with the 0·5 per cent. test-solution, and gradually go down; in case of "pure benzol," you begin with the 0·25 or even the 0·1 test. As already mentioned, the limit of the applicability of the colorimetric method is at 0·05 per cent., for in the just-described method of working in a stoppered flask a percentage of 0·026 does not any more produce a green colour, but merely a faint, grey discoloration of the yellow isatine solution, whilst in the *qualitative* test, carried out as above described in a small porcelain dish, the blue and soon also the green colour appears in any case. With the test solutions of 0·025 and 0·01 per cent. thiophen, these low concentrations can be colorimetrically distinguished also in the dish, by adding to each 25 c.c. of the 0·05 per cent. isatine solution always 1 c.c. benzene-test and the benzol to be examined.

9. *Testing for Total Sulphur.*

Irwin (*J. Soc. Chem. Ind.*, 1901, p. 440) justly contests the assertion made by Holland and Phillips (p. 981), according to which their method indicates the total sulphur contained in benzol, whereas it acts only on carbon disulphide. He therefore proceeds as follows (Fig. 212). Into a spirit lamp, A, holding 100 c.c. he puts 10 c.c. of the benzol with 90 c.c. pure alcohol or methylated spirits (the latter to be tested for sulphur in the same apparatus), shakes up, and lights the lamp. Round the wick he puts some pieces of carbonate of ammonia, F, and covers it with the bent funnel, B, just as is done in the ordinary testing of coal-gas for sulphur. The flame must not be too large, otherwise it will smoke, and no more wick than is absolutely necessary must be used. The gases pass through the apparatus C, filled with moist glass beads, where the sulphur is retained; C is at the end washed out into E, and the sulphuric acid formed is estimated as $BaSO_4$. If we call the weight of the latter n, then the term $\frac{n \times 32 \times 1000}{232 \times 10}$ expresses the number of grams of S per litre. The results are rather too low, but sufficient for practical purposes.

Johnson (*J. Amer. Chem. Soc.*, xxviii., p. 1209) describes an apparatus for burning the benzol vapour in an oxygen atmosphere, absorbing the gases formed in a suitable way, and estimating therein the S in the usual way.

Schenk (*Chem. Zeit.*, xxxviii., p. 83) gasifies the sulphur compounds in commercial benzols by means of a slow current of air, inflames the gaseous mixture of benzols, air and sulphur compounds, and converts the latter by means of hydrogen peroxide into sulphuric acid.

According to Ellerton (*J. Gas Lighting*, 1912, cxvii., p. 222) the typical English commercial benzols contain the following percentages of total sulphur:—Benzol from Durham tar 250 grains per gallon; from Yorkshire tar 240 grains; from Lancashire tar 49 grains; from Staffordshire tar 50·4 grains; crude coke-oven benzol 64·4 grains.

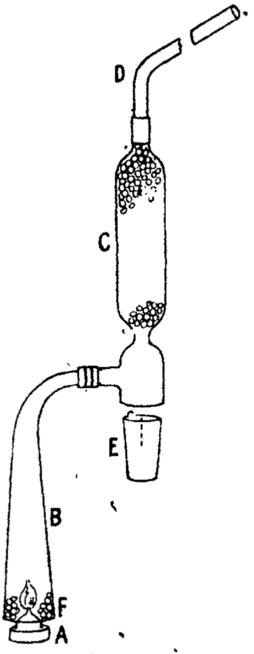


FIG. 212.

10. *Testing for Pyridine and other Bases.*

Commercial 50 per cent. benzol sometimes contains 0·1 per cent. *pyridine*, and the toluene made from this 0·25 per cent. pyridine. This, as well as other basic substances, are detected by agitating 100 parts of benzol with 4 parts of 10 per cent. sulphuric acid for half an hour, separating the acid solution by means of a tap-funnel, making it alkaline with caustic soda, and distilling in a current of steam. The distillate is saturated with nitric acid and evaporated to dryness on a water-bath. Or else, in lieu of distilling, the free bases are extracted from the solution by means of ether. Properly purified benzol ought not to contain anything soluble in dilute sulphuric acid, and but little imparting a dark colour to strong sulphuric acid. Sometimes a maximum is stipulated for the percentage of substances dissolved out by strong sulphuric acid, viz., non-saturated hydrocarbons and thiophene. The former can also be determined by titration with bromine-water. Nitric acid of sp. gr. 1·4 should not produce any white vapours when poured into benzol, and ought not to colour the benzol on agitating.

11. *Estimation of the Real Composition of Commercial Benzols.*

The quantitative estimation of the pure benzenoid hydrocarbons in commercial benzols is sometimes necessary for the objects of the manufacturer of aniline colours, etc., etc. This is possible in consequence of the considerable difference of boiling-points of pure benzene, toluene, the xylenes, and the cumenes.

For this purpose the common retort or fractionating-bulb must be replaced by a more perfect apparatus for fractional distillation, *e.g.*, Linnemann's three-bulb tube, fitted with platinum-gauze cups, or a Le Bel-Henninger three-bulb tube, which is the apparatus most usually employed in England. A Hempel tube, as shown in Fig. 213, is quite as efficient and less liable to breakage; it is a simple tube, narrower at the bottom, and with a side-branch near the top, filled with rough glass beads.

Kreis (Liebig's *Annalen*, ccliv., p. 259) has examined some of the laboratory fractionating-columns for their efficiency.

In Germany, according to the description of Frank (*Chem. Ind.*, 1901, p. 265), a kilogram of benzol is distilled from a copper-retort (as shown in Fig. 214), on which a Le Bel-Henninger column, 2 ft. long, is placed. The thermometer must have an adjustable scale, or else its indications must be corrected by the rules given by Lenders (p. 968). The position of the coolers, its width, and the rate of distillation are adjusted as described lower down. The distillates are collected in tared glass bottles. The single fractions are taken as follows :—

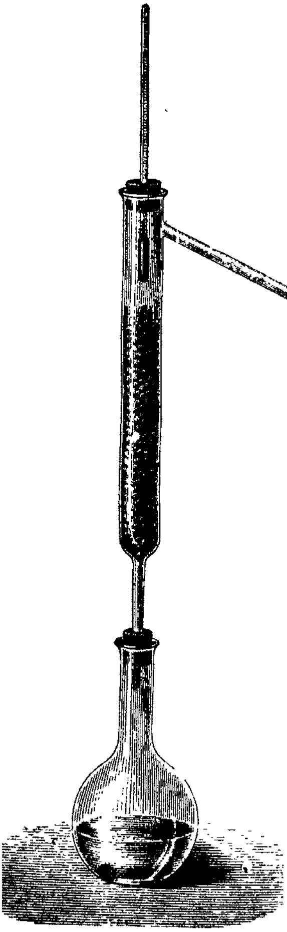


FIG. 213.

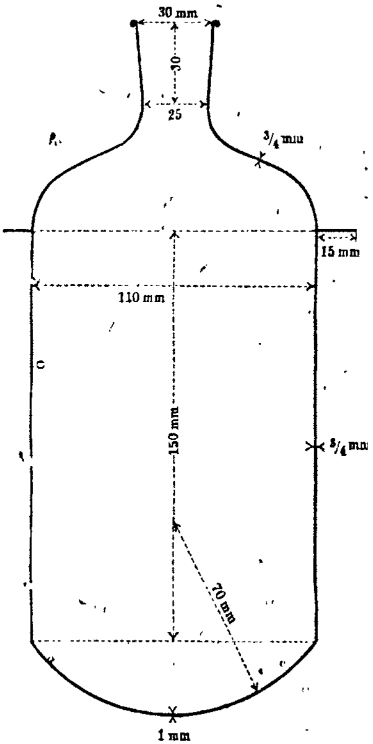


FIG. 214.

(1) With 90 and 50 per cent. benzol:—

First runnings	up to 79° C.
Pure benzene	from 79° to 85°.
Intermediate fraction	„ 85° „ 105°.
Pure toluene	„ 105° „ 115°.
Xylene	over 115°.

(2) With "pure benzol":—

First runnings	up to 79°.
Real benzene	from 79° to 81°.
Last runnings	over 81°.

(3) With "pure toluol":—

First runnings	up to 79°.
Real toluene	from 109° to 110°·5.
Last runnings	over 110°·5.

(4) With xylol:—

First runnings	up to 135°.
p-Xylene	from 135° to 137°.
m-Xylene	„ 137° „ 140°.
o-Xylene	„ 140° „ 145°.
Last runnings	over 145°.

When tested according to these prescriptions, commercial benzols, according to Frank, yield on the average the following results:—

	90 per cent. benzol.	50 per cent. benzol.
First runnings	1·0	0·3 per cent.
Benzene	78·8	18·3 „
Intermediate fraction	10·0	47·5 „
Toluene	8·0	23·7 „
Xylene	2·0	10·0 „
Loss	0·2	0·1 „

	Pure benzol.
First runnings	0·5 p.c.
Benzene	98·0 „
Last runnings	1·2 „
Loss	0·3 „

	Pure toluol.
First runnings	0·3 p.c.
Toluene	97·3 „
Last runnings	2·2 „
Loss	0·2 „

	Xylol.
First runnings	1·3 per cent.
Paraxylene	15·0 „
Metaxylene	76·5 „
Orthoxylene	5·0 „
Last runnings	2·0 „
Loss	0·2 „

Toluene, if present in "chemically pure benzene," is recognized, according to Raikow and Uerkewitch (*Chem. Zeit.*, 1903, p. 295), by nitrating it (*cf.* p. 975 *et seq.*) and adding caustic soda to the product at ordinary temperature. Chemically pure nitrobenzene remains colourless, but even a minute quantity of nitrotoluene produces a yellow-brown colour, especially when the product has been diluted with a little gasoline.

According to *J. Gas Lighting*, 1914, cxxviii., p. 727, and 1915, cxxix., p. 198, the Committee on the Supply of High Explosives have issued a notice to tar-distillers, etc., specifying the standard distillation test for toluene in benzol. The sample is distilled from a flask having a bulb (preferably coppered) of 150 to 180 c.c. capacity, a neck about 5 in. long, and a side-tube about the middle of the neck. A water-cooled condenser, 18 to 20 in. long, is used, and a 100 c.c. graduated cylinder for the distillate. The flask and condenser are washed with the benzol to be tested, and 100 c.c. of benzol introduced. The rate of distillation should be 2 drops per second. When the corrected benzol thermometer shows 90° C. (at 30 in. pressure, or ± 0·1° for ∓ 0·1 in. pressure), the apparatus is allowed to cool, and the distillate is read off. Any deficiency from 100 c.c., when the residue is added to the distillate, is considered as distillate. If the distillate amounts to more than 95 per cent. and the specific gravity of the benzol is between 0·880 and 0·890 at 15° C., it may be sold without a permit, but if the distillate is less than 95 per cent., a sample must be submitted to the Committee for test.

Colman (*ibid.*, p. 196; *J. Soc. Chem. Ind.*, 1915, p. 168) gives a table for ascertaining the percentage of pure toluene in commercial toluol from the percentages of the fractions boiling below 105° and above 117°.

Charitschkow (*Chem. Zentr.*, 1907, i., p. 1738) separates the aromatic hydrocarbons by fractionated precipitation from the alcoholic solution.

A special method for the testing of commercial *xylol*, in order to determine the quantity of the *three isomeric xylenes and of neutral oils*, has been published by Levinstein (*J. Soc. Chem. Ind.*, 1884, p. 77; *cf.* also *supra*, p. 945) based on the behaviour of those substances towards nitric acid, concentrated sulphuric acid, and fuming oil of vitriol. This is very important, since the commercial xylol, although boiling within two degrees, contains the three isomers in very different quantity, while only one of them, metaxylene, is of technical importance. We abstain, however, from describing his method in detail (which had been done in our last edition, pp. 777 and 778); because not merely objections have been made as to its accuracy by Reuter (*Ber.*, 1884, p. 2028), but Levinstein himself only claims "approximate accuracy" for it.

The analyses given by Levinstein are also at variance with the statement by Nölting, Witt, and Forel (*Berl. Ber.*, 1885, p. 2068), that they always found at least 25 per cent. paraxylene in commercial xylol, whilst Levinstein in a dozen samples found only from 3 to 10 per cent. paraxylene.

Radzizewski and Wispek (*Ber.*, 1885, p. 1280) state that very small quantities of paraxylene can be detected in ortho- or metaxylene by treating the hydrocarbons with an insufficient quantity of bromine (*e.g.*, 24 parts bromine to 10 parts of the hydrocarbons); in that case the paraxylene bromide separates first, on cooling, in the shape of a pulverulent precipitate melting at 143°·5.

Compare also the methods of Reuter and of Crafts, described pp. 943 and 944, which are intended for separating the isomers in bulk, and which might be thought of for analytical purposes as well.

Bornstein and Kleemann (*Ber.*, 1891, Ref. p. 486) separate the isomeric xylenes by converting them into xylidines, and utilizing the different behaviour of these towards dry sulphur dioxide.

Weger (*Z. angew. Chem.*, 1909, p. 341) does not consider Levinstein's method to be accurate (which is not claimed by its author himself; *vide supra*). He is not aware of any satisfactory analytical method for the separation of the three xylenes.

Northall-Laurie (*Analyst*, xl., pp. 384-389; *J. Soc. Chem. Ind.*, 1915, p. 350) describes in detail the estimation of toluene in commercial toluol.

Friedel and Crafts (*Comptes rend.*, ci., p. 1218) describe a method for separating *ethylbenzene* from orthoxylene.

A method for separating the two *trimethylbenzenes* (pseudocumene and mesitylene) has been described by Jacobsen (*Ber.*, 1876, p. 256). It is founded upon converting them into sulphamides.

separating these by alcohol, and regenerating the hydrocarbons by fuming hydrochloric acid. Up to the present time no technical use has been found for this method.

12.—*Practical Tests in the Laboratory for Final Products obtainable on a Larger Scale.*

At one of the largest German aniline works the following process is employed for testing commercial benzol:—(1) *Preliminary test*—Twenty c.c. pure concentrated sulphuric acid is shaken with 1 c.c. benzol in a stoppered bottle, and allowed to stand for twelve hours. The colour ought not to be more than light yellow. (2) *Purification*—One thousand g. benzol is shaken with 125 g. concentrated sulphuric acid for half an hour in a large drop-funnel. If in the preliminary test the colour was strongly yellow, more acid, up to 200 c.c., must be taken. After settling, the acid is drawn off, the benzol shaken up three or four times with 200 c.c. water each time, and again three or four times with 1 per cent. caustic-soda solution. Now 10 c.c. of the benzol is shaken with successive portions of 0·5 c.c. saturated bromine-water, until the benzol retains its yellow colour at least for two minutes. It is then poured back to the main portion. If more than 1·5 c.c. bromine-water has been used in this test, the sulphuric-acid washing should be repeated with another 50 c.c. of acid, and this again repeated until in the above test no more than 1 or 1·5 c.c. bromine-water is used. The washed benzol is now dried by occasionally shaking up with fused calcium chloride for two hours, and the loss by the purifying process is ascertained by weighing it. (3) *Fractionating*—The purified benzol is put into the copper retort K, Fig. 215, placed on a tripod, D. The cover M is screwed on; it is provided with an opening for the thermometer T_1 and the Le Bel-Henninger fractionating-head F. The latter (in two pieces) consists of 12 bulbs, with platinum-wire gauze in each, and measures up to the side-tube R. In the top the thermometer T_2 is fixed so that the bulb is just on a level with the lower part of the side-tube R, which is connected with a Liebig cooler, L, 1 metre long. The distillation is carried on by means of a Bunsen burner, in such a manner that two drops fall per second. The distillates are collected in tared receivers and weighed

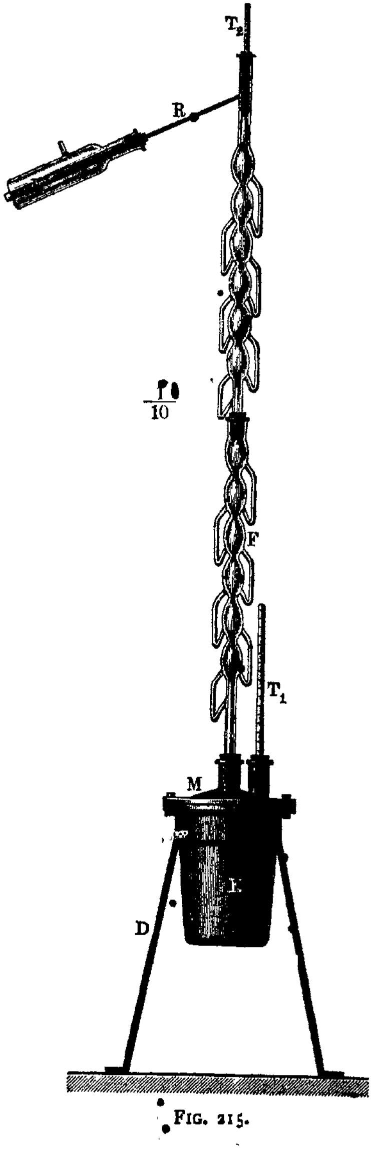


FIG. 215.

The fractions are made as follows:—(*a*) for 90 *per cent. benzol:* first runnings, up to 79°; benzene, 79° to 85°; intermediate fraction I., 85° to 105°; toluene, 105° to 113°. When 113° has been reached, the distillation is interrupted and the residue in the retort is weighed; (*b*) for 50/90 *per cent. benzol* and 0/90 *per cent. toluol:* first runnings, up to 79°; benzene, 79° to 85°; intermediate fraction I., 85° to 105°; toluene, 105° to 113°; intermediate fraction II., 113° to 133°. At 133° the distillation is interrupted, the residue is weighed and treated with steam, and weighed again as "residue." The loss found by adding up the residue and all the fractions is "loss in distillation." In reporting the results, 85 per cent. of the first runnings is calculated as benzene, 60 per cent. of intermediate fraction I. as benzene, and 40 per cent. as toluene. For the intermediate fraction II. no fixed proportion has been ascertained. (4) *Estimation of aliphatic hydrocarbons.*—One hundred g. benzol is nitrated (*cf.* p. 975) with 125 g. sulphuric acid (1·84) and 125 of nitric acid (1·5) at not more than 30° C. The crude nitrobenzol is separated from the acid, neutralized with caustic soda, and distilled with steam until a sample of the distillate sinks in water. The distilled oil is separated from water and placed in a narrow graduated cylinder (50 c.c.), where from 15 to 40 c.c. of the above acid mixture is gradually and carefully added, with occasional shaking, until the volume of the oil ceases to diminish. By this treatment any unchanged benzene and toluene are dissolved in the acids; the aliphatic hydrocarbons float on the top and their volume is read off. This is calculated as amounting to 60 per cent. of the actually present fatty hydrocarbons. This test is only made if there is reason to expect a somewhat large proportion of aliphatic hydrocarbons from the results of the purifying test.

Claudon and Morin (*Bull. Soc. Chim.*, xlviii., p. 804) describe a small-scale column-apparatus (Figs. 216 to 219) for fractionating spirit, benzol, etc., which is quite similar to the large-scale apparatus, and which I can recommend from practical experience. A (Fig. 216) is a double-ring gas-furnace. The bottom of boiler B is slightly inclined towards tap M, to facilitate emptying. N is a charging hole, with funnel, O, to fit in. Tube L is a liquor-gauge; K (of which the details are shown on a larger scale in Fig. 217) a pressure-gauge.

Column C contains 10 plates, like the sieve-plates of large apparatus, easily cleaned and removed. The inner cooling-pipe I receives water from P, and the warm water runs off at Q. The "analyzer" D, with thermometer *t*, catches any froth and returns it to the column. E is an ordinary cooler. The overflow vessel F (shown also in Fig. 219) admits of checking the specific gravity of the distillate by a hydrometer, *a*, and of taking samples at *b*. From here the distillate runs through funnel *b* and pipe *a* (Fig. 218) into bottle G. When this is full, float *c* rises and closes the contact *l m*, leading by *i k* to an electric bell. Rod *c* (Fig. 217) of the pressure-gauge K (Fig. 217) slides in a copper collar, *b*, and is fixed by screw *d*. When the pressure in the boiler rises above a certain height, the mercury in the gauge rises as well, and a platinum wire at the

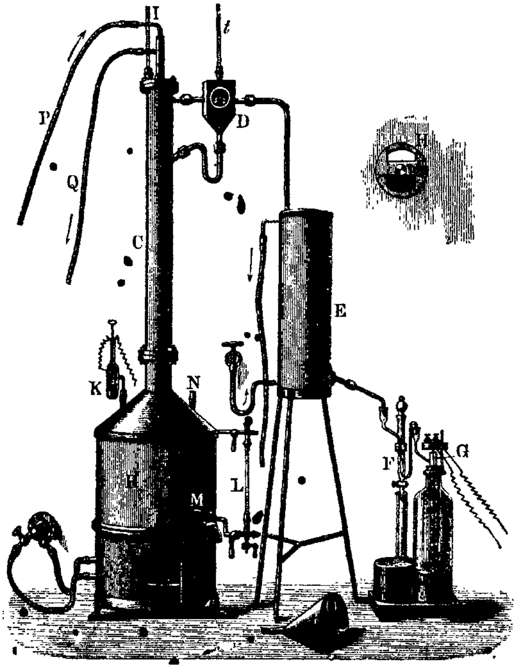


FIG. 216.

bottom of *c* comes into contact with an electric bell, by means of *a*, *g*, *f*, and *e*. This is only required where several such apparatus are going at the same time. The distillation must be carried on slowly at the commencement, till all the plates are filled and the cooling-water is regulated.

A paper on the valuation of crude naphtha, etc., has been published by G. E. Davis (*J. Soc. Chem. Ind.*, 1885, p. 654). He mentions that the method usually employed is to distil a quantity (generally 100 c.c.) in a tubulated glass retort, and to catch the quantity distilling over up to a temperature of 120° C., the bulb of the thermometer being immersed the whole time in the boiling liquid. The article is generally sold on the basis of an average yield of 30 per cent. at 120°, within a rising or falling allowance per degree, or every 1 per cent., within prearranged limits. This test has nothing to recommend it except its simplicity; and if buyers do not receive a sample, so

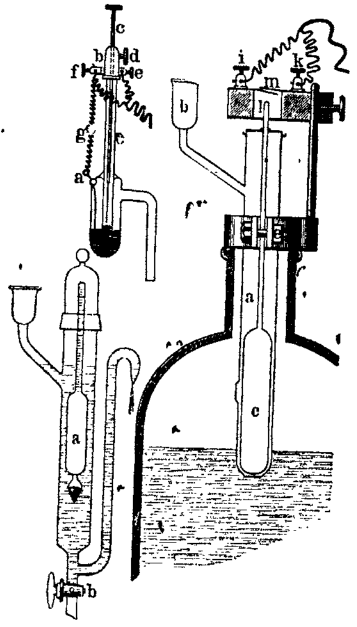


FIG. 217.

FIG. 219.

FIG. 218.

as to judge for themselves, but only an account of the test, they may suffer great losses. Crude naphtha is valuable only for the benzene, toluene, and solvent naphtha it contains; but the distillation-test to 120° does not differentiate these products, nor does it take any account of the loss in washing with acid and alkali. A much better test than the above is:—One hundred c.c. of the naphtha is distilled in a 200 c.c. flask, with a thermometer arranged so that the bulb is just off the bottom of the flask. The distillate is caught in a 100 c.c. graduated cylinder, and the yield taken at the following points: 100°, 110°, 120°, 140°, 170°, 200°. The quantity which has passed over at 140° is again distilled, and the yield at 100° and 120° noted. [This almost exactly agrees with the prescription given by me so far back as 1867.] All that passes over up to 100° in the second distillation is called *benzol* (B); that which passes between 100° and 120° in the second distillation is called *toluol* (T). *Best naphtha* (N_1) is that which passes between 120° in the second and 170° in the first distillation; *second naphtha* (N_2), that caught between 170° and 200° in the first distillation; and *creosote* (C), the balance. The following are some tests made by this method:—

Spec. grav.	First distillation.						Second.		Products.				
	100°	110°	120°	140°	170°	200°	100°	120°	B.	T.	N_1.	N_2.	C.
0·886	2	22	42	67	88	94	23	53	23	30	35	6	6
0·893	11	30	50	72	88	95	27	56	27	29	32	7	5
0·903	2	14	23	56	78	92	23	42	23	19	36	14	8
0·915	0	2	11	39	73	94	7	26	7	19	47	21	6
0·917	2	16	34	57	75	87	22	43	22	21	32	12	13
0·940	2	10	21	42	59	69	23	36	23	13	6	17	10

This method is, however, not yet accurate enough. The redistillation of a large quantity of the different fractions gave the following results:—

B . .	85°	90°	95°	100°	110°	120°
	2	48	71	80	90	95 per cent.
T . .	100°	110°	120°	130°	135°	
	47	75	86	94	96 per cent.	
N_1 . .	130°	140°	150°	160°	170°	180°
	13	43	63	79	91	93 per cent.
N_2 . .	160°	170°	180°	190°	200°	
	2	31	55	74	87 per cent.	

The "creosote" crystallized into a solid mass [probably naphthalene]. The above shows that the "benzol" is only of a strength of 80 per cent., the "toluol" is nearly a 50 to 90 per cent. benzol, the naphthas N_1 and N_2 are mixtures of solvent-naphtha and light oil. Neither does the just-described method take into account the products eliminated by washing with acid and soda. In a special case 1600 gall. of crude naphtha, tested by that method, yielded :—

25 B, 23 T, 32 N_1, 10 N_2, 10 C.

After washing there remained 1200 gall., which tested :—

26 B, 14 T, 24 N_1, 9 N_2, 27 C.

When this quantity was worked in a still of the best construction it yielded :—

348 gallons	90 per cent. benzol	= 23	per cent.
362	50 per cent. benzol	= 24	„
156	solvent-naphtha	= 10	„

Hence the test would have led one to suppose that much more solvent-naphtha [and less 50 per cent. benzol] would be obtained than was actually the case.

Davis therefore recommends the following method [which practically agrees with the general prescriptions given by myself in the first edition of this work, pp. 251 and 252] :—

Two hundred c.c. of the crude naphtha are agitated with 20 c.c. concentrated sulphuric acid (rectified oil of vitriol) in a stoppered globular separating-funnel of 300 c.c. capacity. After agitating well for five minutes, allow to settle and run off the acid carefully, so that nothing is lost. (Sometimes two washings with 10 c.c. of acid each are preferable to one washing with 20 c.c.) Now wash twice with 30 c.c. of water, each time running off the wash-waters very carefully, then add 30 c.c. caustic-soda solution, of sp. gr. 1·060, and again wash with water. Pour the washed naphtha into a measuring-jar, and determine the percentage loss. All is now ready for the distillation. Measure off 100 c.c. of the washed naphtha, less the percentage loss, and place in a 200 c.c. flask fitted with a delicate thermometer and

Glinsky's or Le Bel-Henninger's fractionating tubes (p. 994, or any other, preferably Hempel's glass-bead tube, which has been shown in Fig. 213, p. 990), connecting it with a Liebig's condenser of the ordinary pattern. Heat the flask with a rose-burner (Fig. 206, p. 959), and so regulate the flame that a drop distils over about once in every two seconds. Carry the distillation on until the thermometer has risen to 120°, catching the distillate in a graduated jar. At this point change the receiver, and catch all that comes over up to 170°. The distillate to 120° consists substantially of benzene and toluene; the portion distilling between 120° and 170° is solvent-naphtha, the remainder creosote. The "solvent" produced in this small apparatus will show the first drop at 125° and 90 per cent. at 100°, which is usually the quality worked for on the large scale. The composition of the distillate to 120° will vary somewhat with every sample of crude naphtha operated upon. In Davis's own case the quantities yielded by each analysis were collected from many examples; and when mixed and tested in the usual way employed for 90 per cent. and 50 per cent. benzols, showed 64 per cent. at 100° and 93 per cent. at 120°. Davis states that it is easy, by means of this method, without any supervision, to run the specified quantities of 90's and 50's from the still direct, without any fear of mistakes. The following table shows the results of the older methods compared with those of the new method:—

Spec. grav.	Old method.	Improved method (p. 999).					Davis's new method.				
	Per cent. at 120°.	B.	T.	N_1.	N_2.	C.	Loss in washing.	Per cent. at 120°.	Test at 100°.	Per cent. solvent.	Creosote.
									Per cent.		
0·886	42	23	30	35	6	6	13·5	50	60	23	27
0·902	31	19	22	35	15	9	18·5	46	59	19	36
0·908	29	17	23	39	13	8	10·5	45	64	23	32
0·924	32	30	13	27	15	15	16·5	47	58	13	40

In order to rapidly estimate the quantities of 90 per cent. and 50 per cent. benzol and toluol which can be run from the still, Davis has constructed the following tables:—

A. Mixtures of 90 per cent. benzol with 50/90 per cent. benzol.

90 per cent.	50 to 90 per cent.	First drop.	Per cent. at 100°.	Per cent. at 120°.
0	100	92°	50	90
5	95	92°	51	92
10	90	91°	51·5	92
15	85	91°	53	92
20	80	90°	55	92
25	75	90°	60	93
30	70	90°	65	93
35	65	90°	67	94
40	60	88°	69	94
45	55	88°	70	94
50	50	87°	71	94
55	45	87°	73	94
60	40	86°	76	95
65	35	86°	78	95
70	30	86°	79	96
75	25	85°	84	96
80	20	85°	84	97
85	15	84°	86	97
90	10	84°	88	dry
95	5	84°	89	dry
100	0	84°	90	dry

B. Mixtures of 50/90 per cent. benzol and commercial toluol.

50 to 90 p. c. benzol.	Toluol.	First drop.	Per cent. at 100°.	Per cent. at 105°.	Per cent. at 110°.	Per cent. at 200°.
100	0	92°	50	68	80	91
95	5	93°	45	64	76	91
90	10	94°	33	60	73	90
85	15	94°	30	58	73	90
80	20	95°	28	57	72	90
75	25	95°	26	55	71	90
70	30	96°	22	48	67	90
65	35	96°	19	47	65	90
60	40	96°	15	46	55	90
55	45	97°	12	44	65	90
50	50	98°	8	42	64	90
45	55	98°	4	34	57	90
40	60	99°	0	26	56	90
35	65	100°	0	25	55	90
30	70	100°	0	23	53	90
25	75	100°	0	21	53	90
20	80	100°	0	16	48	90
15	85	101°	0	14	46	90
10	90	102°	0	13	45	90
5	95	103°	0	10	44	90
0	100	103°	0	0	39	90

C. Mixtures of 90 per cent. benzol with commercial toluol.

90 per cent. benzol.	Toluol.	First drop.	Per cent. at 100°.	Per cent. at 105°.	Per cent. at 110°.	Per cent. at 120°.
0	100	103°	0	7	50	94
5	95	102°	0	21	59	94
10	90	101°	0	30	66	94
15	85	100°	0	38	68	95
20	80	97°	9	43	73	95
25	75	95°	16	53	76	95
30	70	95°	23	59	78	96
35	65	94°	43	60	80	96
40	60	93°	43	66	82	96
45	55	92°	46	71	85	97
50	50	91°	52	72	86	97
55	45	91°	58	76	86	97
60	40	91°	60	78	88	97
65	35	90°	65	81	89	97
70	30	89°	71	83	91	97
75	25	88°	75	85	91	98
80	20	87°	77	87	92	98
85	15	86°	83	89	93	98
90	10	85°	85	91	94	dry
95	5	84°	88	93	95	dry
100	0	84°	90	94	96	dry

The *pecuniary valuation of crude naphtha* can be easily made, if the proper test has been applied. Davis quotes the following example. A sample, tested by his new process, yielded :—

Loss by washing	$18\frac{1}{2}$ per cent.
Distillate to 120°	45 per cent.
Test of same $\frac{100^\circ}{71}$ $\frac{120^\circ}{94}$.	

[*i.e.*, 50 per cent. of 90 per cent. and 50 per cent. of 50 per cent. benzol, according to table A.]

Distillate to 170° . . .	10 per cent.
Test of same $\frac{126^\circ}{0}$ $\frac{160^\circ}{92}$.	

The quantities actually obtained from the still were :—

90 per cent. benzol 23 per cent. at 1s. 7d., f.o.b. Goole, casks free.
50 per cent. benzol 24 per cent. at 1s. 4d.
Solvent . . 10·4 per cent. at 9d.
Test of solvent $\frac{130^\circ}{1}$ $\frac{160^\circ}{94}$.
Loss by washing, 20 per cent.

Deducting 2d. per gall. for barrels, 2d. for carriage, and 1d. for sundries (leakages, super tares, etc.), this leaves at the works:—

90 per cent. benzol 23 gall. at 1s. 2d. = 322d.
50 „ „ 24 „ 11d. = 264d.
Solvent . . 10 „ 4d. = 40d.

$$\frac{626}{100} = 6\tfrac{1}{4}\text{d.}$$

per gallon of crude naphtha, out of which the rectifier will have to find (apart from the price of the crude naphtha) vitriol, soda or lime, wages, steam, repairs, depreciation, sundry charges, and his profit, if there be one.

Methods of Lunge.—Usually much less complicated methods than Davis's are employed for testing crude naphtha for its commercial value. The following empirical rules are taken from my own practice, and by means of them the results to be expected on the large scale can be very approximately inferred from laboratory distillations, which will take hardly a quarter of an hour. They were elaborated before fractionating-bulbs had come into use, but they still hold good.

1st. One hundred c.c. of the oil is distilled from a glass retort or fractionating-flask, and the distillate collected, (*a*) up to 140°, (*b*) from 140° to 170°. On each occasion, just as the required temperature is attained, the lamp is withdrawn, and the oil contained in the condenser is allowed to drain off before the receiver is changed; this makes a difference of several per cent. Suppose we have got 68 c.c. up to 140° and 86·5 c.c. up to 170°,—

2nd. The first distillate, in this case 68 c.c., is rectified, and that which passes over up to 100° is collected, allowing the oil to drain after removing the lamp. Suppose this to be 24 c.c. This figure, multiplied by 2, gives the quantity of 50 per cent. benzol to be expected; in this case it is 48 parts from 100 parts of the crude oil.

3rd. The product (*a*) of the first distillation (up to 140°), in this case 68 c.c., less the 50 per cent. benzol found according to rule 2, in this case 48 c.c., gives the volume of best naphtha, *i.e.*, 68 − 48 = 20.

4th. The total product of the first distillation up to 170°, in this case 86·5 c.c., diminished by 15 per cent. for loss by purification (washing) and distillation, and by the quantities of 50 per cent. benzol and best naphtha found according to rules 2 and 3, gives the quantity of burning-naphtha. In this case, $86{\cdot}5-13=73{\cdot}5$; $73{\cdot}5-68=5{\cdot}5$ parts for 100 crude naphtha. (A loss of 15 per cent. may be regarded as a maximum; with careful work it does not exceed 10 per cent.)

5th. The difference is the residue going to creosote oil. Thus in our case we find the following total:—

48	parts	50 per cent. benzol
20	„	best naphtha
5·5	„	burning-naphtha
15	„	loss
11·5	„	creosote oil
100·0		

If less volatile oils have to be tested, 200 or 300 c.c. are distilled up to 180°, and the residue is submitted to exactly the same operations and calculation-rules as have just been described.

At the present time most tar-distillers test their crude naphtha by means of fractionating-bulbs (Le Bel's, Hempel's, etc.), and thus obtain results very nearly indicating the probable yield on a large scale.

Spilker (Muspratt's *Chemie*, 4th ed., sub. *Steinkohlenteer*) gives the following prescriptions for estimating the yield of purified products from the crude benzol of coke-ovens, or from the light oil of tar-distillers, which have stood the practical test very well.

1. *Titration by Bromine.*—Two kg. of the well-mixed sample are distilled in a tared copper still, holding 2½ to 3 litres and provided with a top-column, 20 cm. long, filled with beads, until the thermometer fixed in the upper part of the column shows 175°. The velocity of the distillation ought to be 8 to 10 c.c. per minute. The residue remaining in the still is weighed, and calculated as "heavy tar-oil." The distillate, after removing any water carried over, is once more distilled as before. This time the state of the barometer must be taken into account, preferably by employing a thermometer with movable scale, fixed immediately before by means of boiling water (steam).

In this second distillation three fractions are collected in tared glass bottles, viz.:—

Fraction I. up to 105° = crude benzol I.
„ II. „ 115° = crude toluol.
„ III. „ 150° = crude solvent-naphtha.

The residue is weighed and added to that obtained in the first distillation. In every one of the three fractions the *loss by chemical washing* is ascertained as follows, and deducted:—

Five c.c. of the fraction are pipetted into a stoppered glass bottle, holding about 150 c.c., in which beforehand 10 c.c. dilute sulphuric acid (20 per cent. H_2SO_4) have been placed. From a burette so much semi-normal solution of potassium bromate+bromate (containing 40·5835 g. KBr+13·9165 g. $KBrO_3$ per litre) is run in, as quickly as possible, until the bromine set free is no more decolorized by the benzol, and this, after shaking for five minutes and standing for ten minutes, just shows a reddish-brown colour. The final point of the reaction is recognized still more accurately by taking out, after the time just prescribed, a drop of the benzol by means of a glass rod and placing it on freshly prepared, moist, zinc-iodide paper, where it produces at once a dark blue spot. For obtaining reliable results, a preliminary test is made in order to fix approximately the required quantity of bromine solution. From the following two exact tests the average is taken, and calculated as loss by washing. Every cubic centimetre of bromine solution, required by the 5 c.c. benzol, in normal cases corresponds to a washing loss of 1·00 per cent. by weight.

2. *Washing Test.*—Two kg. of the sample is distilled in the copper still as described *sub* No. 1. The distillate, after removing any water, is placed in a tap-funnel, holding about 2½ litres, and washed twice with about 10 vol. per cent. of caustic-soda solution, sp. gr. 1·1, and then with 10 vol. per cent. of sulphuric acid, sp. gr. 1·33, always shaking it for five minutes.* The aqueous liquids, after settling, are completely removed. The fraction, thus freed from acid and basic impurities, is twice very vigorously shaken with each time 3 vol. per cent. sulphuric monohydrate during fifteen minutes, allowed to settle for fifteen minutes, and the acid carefully drawn off. The acid should be added every time in three

portions in short intervals. In conclusion, the benzol is washed, first with 1 per cent. water and then with caustic-soda solution, up to neutral reaction. The last portions of aqueous liquid are removed by pouring the benzol into a copper still, holding about 2 litres, and distilling in the same way as the first time (taking account of the barometric pressure), collecting the following fractions in tared stoppered glass bottles:—

Fraction I. up to 105° = 90 per cent. commercial benzol.
„ II. „ 115° = purified toluol.
„ III. „ 150° = solvent-naphtha.

Here also the weights of the fractions, after removing the water, indicate the contents of the 2 kg. of raw material employed in commercial products.

The three fractions must be tested for their reaction against sulphuric acid and bromine. If this reaction does not agree with that prescribed for typical commercial products, another test must be made, employing more sulphuric acid, until the demands made by the commerce are satisfied.

Storage and Carriage of Benzol, Naphtha, etc.

In a former place (p. 884), we have described the precautions which must be taken in the erection of the localities in which light tar-oils are to be treated and stored, on account of the danger of fires and explosions, and to these we must refer in this place as well.

For storing benzol and naphtha, only wrought-iron vessels are suitable; they may be of any shape and size. Since tar-oils pass through the joints much more easily than water, both as liquids and as vapour, and since their vapours form with air readily inflammable or even explosive mixtures, the store-tanks must be constructed with special care and should be protected against any contact with fire. They are put together in as large plates as possible, to lessen the number of joints; and these are very carefully riveted and caulked. Only first-class workmanship will ensure that no evaporation takes place. The tanks are painted outside with good tar-varnish (pp. 548 *et seq.*), but preferably not until the joints have somewhat rusted and have thus become tighter. They are provided with a hole for filling them, a manhole, and two taps—one a little above the bottom for the ordinary filling of the sending-out vessels, the other in the bottom itself, for occasionally drawing off any water and mud. The tanks are mostly placed on pillars high enough to fill the casks directly. But at some works tanks placed in the open air, and partially underground, are preferred, on account of the diminished danger of fire. In any case, for the same reason, the benzol storehouse should be at some distance from any fireplace; and it is best to employ an open shed for it. Artificial lighting of the benzol storehouse is mostly unnecessary; in case of need, this must be done only from the outside by means of reflectors.

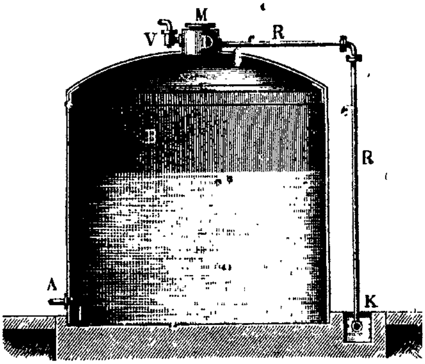


FIG. 220.

Hausmann (Ger. P. 90368) describes a suitable kind of reservoir for this and similar purposes. The tank B, Fig. 220, has a dome, D, and a manhole, M. From D branches off pipe R to a water-vessel K; on the other side a back-pressure valve, V, is fixed, which allows air to get in, but no gas or vapour to escape. When B is being filled through A, the air escapes through K, where the vapours are condensed and gases escape. If they should take fire, the water-lute prevents it from being communicated to the inside of B. During the emptying of the tank, air enters gradually through V.

In order *to prevent the formation of explosive mixtures* of benzol vapours and air, various inventors (as proposed first by Bunte) prescribe displacing the air in the storage vessels by carbon dioxide or gases containing a large proportion of this. Martini and Hüncke (Ger. Ps. 146161, 149086, 150712, 151730) keep benzin, etc., in underground reservoirs under the protection of non-oxidizing gases, so that there is no possibility of forming explosive mixtures of the hydrocarbon vapours with atmospheric oxygen. These gases also serve for transporting the liquid without a pump, etc., to the running-off valves. All the conduits, fittings, and valves are surrounded by jackets, and the annular spaces thus formed are connected with the reservoirs, so that the gaseous pressure existing in these is continued up to the running-off valves. A plant constructed on this principle, mounted in the Spree harbour at Berlin, comprises 36 store tanks with a total capacity of 1,000,000 litres, placed 3 ft. underground. *Cf.* Rosenthal, *Z. angew. Chem.*, 1911, p. 289.

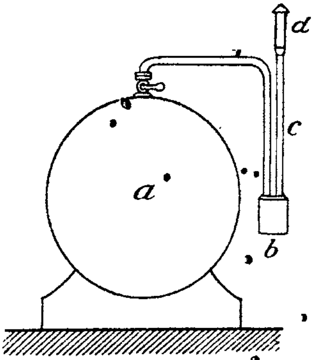


FIG. 221.

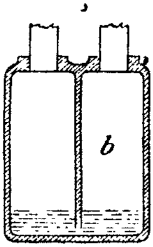


FIG. 222.

Other safety apparatus for easily inflammable liquids have been constructed by Mund (Ger. P. 149927).

The Aktien-Gesellschaft für Anilinfabrikation at Berlin, according to *Chem. Ind.*, 1902, p. 491, has provided its benzol tanks with the safety arrangement shown in Fig. 221, which seems to be very efficient for its purpose. The tank *a* is by means of a pipe connected with vessel *b*, which is shown on a larger scale in Fig. 222. *b* is divided into two chambers by a partition not reaching quite to the bottom, the opening being luted by glycerine. One chamber of *b* is connected with *a*, the other chamber with the outer air by means of pipe *c* with the cap *d*.

The latter is filled tightly with thin rods of iron, in order to prevent any flame of benzol vapours, burning at its top, from getting back into *a*.

In this connection the proposals made of issuing Rules of Safety for establishments using benzin (*i.e.*, petroleum spirits) for cleaning purposes, published in *Chem. Ind.*, 1902, p. 369, are of some interest; also the paper of Effenberger, in *J. Gasbeleucht.*, 1906, p. 689.

Some proposals aim at preventing explosions of store- and carriage-tanks for benzol, benzin, spirits of wine, etc., by providing the vessels with safety-valves of special constructions. To these belong the apparatus "Hofmann," invented by F. Schmitt, and sold by the Fabrik explosionsicherer Gefässe.

Other proposals are made for making benzole uninflammable, *e.g.*, for chemical-cleaning purposes, by certain additions.

Lyndall and Costley-White (B. P. 16756, 1904) recommend for this purpose the addition of carbon tetrachloride, of which, however, too much is required to entirely remove the inflammability, according to several observers.

Dilette and Talabot (Fr. P. 341927) mix benzol with 15 per cent. carbon tetrachloride, in order to make it uninflammable.

Devinet (*Chem. Zeit.*, iv., p. 219) asserts that the addition of $\frac{1}{3}$ volume of carbon tetrachloride makes benzol uninflammable in storing and using as a detergent. Pfister (*Z. angew. Chem.*, 1905, p. 1786) states that twice the volume of carbon tetrachloride of that of benzin is required for this purpose.

Barboni (Fr. P. 350313; B. P. 1202, of 1905) makes benzol uninflammable by chlorinating with addition of carbon disulphide and iodine, and subsequent distillation over brimstone. [This proposal is anyhow not applicable to tar benzol.]

H. Hoffmann, Apparatebau-Ges. m. b. H., Frankfort (B. P. 12128, of 1914), causes the air, which enters the storage vessel to replace the liquid withdrawn, to bubble through a small chamber filled with the inflammable liquid, whereby it becomes saturated with the vapour to such a degree that a non-explosive mixture is formed. When the storage vessel is being filled with inflammable liquid, the air which is expelled escapes without passing through the saturator.

The *carriage* of benzol is best effected in iron tank-wagons or iron casks. Formerly, but nowadays only exceptionally, wooden casks were employed, *e.g.*, spirit-puncheons, which for this purpose must be made tighter by washing with a thin, hot solution of glue, like petroleum barrels. The glue may be ordinary animal glue, or, according to Graefe ("Braunkohlenteer-Industrie," p. 96), the so-called "natural gum," which is a product obtained from molasses; or else glue hardened by chrome. The casks are first steamed out; then 1 or 2 litres of glue solution are run in; the casks are moved about so that their inside is evenly wetted, and the excess of glue solution is run out. Before use, the casks are dried by prolonged keeping in a warm place, or blowing in of hot air. After drying they are filled with benzol, leaving an empty space of 2 in. in the winter season, or 3 to 4 in. in summer, in order to allow for the expansion of the benzol by higher temperatures during transit. This precaution must also be taken in the case of iron vessels.

For the momentary stoppage of leaks, soap can be employed which is not acted upon by naphtha; but it does not stand any considerable pressure. Glue, too, is not acted upon.

For *moving about benzol* in the factories, *compressed air* is very much in use as a matter of course. Explosions have occurred in this process which are attributed by some to the formation of electric sparks; but it is more likely that the formation of iron sulphide from the sulphur compounds in crude benzol gives rise to such an elevation of temperature that benzol, toluol, and even higher homologues are inflamed. (*Cf.* Oehler, *Chem. Zeit.*, xxviii., p. 1133; Roesler, *ibid.*, p. 1237; Ernst, *ibid.*, p. 1201; Rasch, *Chem. Centr.*, 1905, ii., p. 1056.) In consequence of this, it is stated by Klocke (*Chem. Zeit.*, xxix., p. 735) that many factories have given up the use of compressed air for moving about the tar-oils, but this is not necessary, if instead of common air, gases with about 12 or 13 per cent. CO_2 (chimney gases) are employed.

An apparatus for automatically and safely filling casks, etc., with benzol, etc., constructed by P. Schnorrenberg, is sold by the Deutsche Wassergas-Beleuchtungs-Gesellschaft in Berlin. It is worked by water under high pressure, which forces the benzol through a closed vessel, containing a float, so regulated that it is not lifted up by the benzol, but by the specifically heavier water. When this takes place, the float is pressed tightly against a valve, thus automatically closing the communication between the store vessels and the transportation cask.

Applications of Benzol and Naphtha.

By far the greatest part of the various commercial benzols (from "90 per cent. benzol" downwards) is used in the manufacture of *aniline colours*, mostly in the shape of amido- and hydroxy-derivates, as well as in that of pure benzene, toluene, and xylenes, and of sulphonic acids. The designation "aniline colours" must, of course, be taken in the widest sense, comprising a vast number of synthetically produced organic colouring matters. More recently, but also to a vast extent, the benzols serve as the first raw material for the manufacture of *artificial scents*, *sweetening matters*, *medicinal preparations*, *explosives*, and *photographic articles*.

We cannot in this book enter upon this vast field, but we will now discuss the application of benzols, etc., to other than the just-named purposes, so far as this has not yet been done in previous chapters, more particularly those of recent date which possess special importance for the future of the industry of benzols.

As *solvents*, benzols have been used from the very first of their technical extraction. We have, on pp. 919 *et seq.*, spoken of the preparation of "solvent naphtha," which has received this name just on account of this property. Probably the oldest of these applications is that introduced by Macintosh in the manufacture of *indiarubber goods*. In this, as well as in most other cases where benzol and its homologues serve as solvents, it would be too expensive, and sometimes even objectionable on account of too great volatility, to employ products consisting mainly of benzene and toluene, such as form the staple article required for colour-making. Hence the cheaper products distilling at a somewhat higher temperature, and essentially consisting of the three xylenes, along with some trimethyl-benzenes, etc., are specially collected and sold as "solvent-naphtha."

We have seen on p. 920 what are the special requirements of English indiarubber manufacturers, whose process has been described by Kniess (*Dingl. polyt. J.*, cxxxviii., p. 442). Since it now pays to extract the xylenes for the manufacture of colours, the solvent-naphtha is of different quality to what it used to be, and such naphtha is hardly so valuable for indiarubber manufacture as the old article (*J. Soc. Chem. Ind.*, 1884, pp. 81 and 82). Heeren (*Dingl. polyt. J.*, ccxxi., p. 391) gave a table of the solubilities of different descriptions of indiarubber in "benzol," which shows variations of from 6 to 25 parts of indiarubber to 100 of "benzol." But whether he means pure benzene, or commercial benzol, or solvent-naphtha, does not appear.

According to Frank and Markwald (*Gummi-Zeit.*, 1903, No. 36) the tar-oils employed for dissolving indiarubber ought to consist of the xylol fractions, which yield 90 per cent. on boiling between 130° and 150° or 160°. Still better than this is the xylol itself. They must not possess a stinging odour.

According to the same authors, commercial 90 per cent. benzol can advantageously replace carbon disulphide in the "cold vulcanization" of indiarubber. This has been carried out in most British indiarubber-works. According to information received by them, in Manchester from 6 to 8 tons benzol are applied to this purpose. In Germany the employment of carbon disulphide is still very common.

To this class of uses of benzol belong also the German patent, No. 124973, of Thornton and Rothwell for making tissues, paper, etc., water-tight by treating with a solution of the salts of zinc with fatty or resinous acids in benzol. Quite on the same lines are the German patents, No. 127582, of Baswitz, and No. 129450, of Serbowski.

Benzol is also largely used as a solvent in the manufacture of *colours*. Of the greatest importance is its pre-eminent dissolving-power for *fatty matters*, upon which is based its extensive employment as a *detergent*; but petroleum "benzin" or "benzoline" largely competes with coal-tar benzol in this respect.

A good domestic detergent consists of a mixture of 25 parts benzol, 5 ether, and 5 absolute alcohol. A detergent for removing fat-, tar-, resin-, wax-, and acid-spots from all kinds of fabrics is prepared by adding 10 parts of benzol to 100 parts of 95 per cent. alcohol, and 35 parts of liquor ammoniæ of sp. gr. 0·875. "Benzol-magnesia" (that is, burnt magnesia soaked with benzol) is excellent for removing grease-spots from fabrics, ivory, etc.

Herzfeld and Beer (Ger. P. 101414) find that an addition of 8 or 10 per cent. benzol increases the solvent power of 96 per cent. spirit of wine for petroleum from 10 or 12 per cent. to 20 per cent., and a further addition of 4 per cent. naphthalene brings up the solubility to 23 or 24 per cent.

Freyfs (*Chem. Zeit.*, 1903, p. 1137) reports on the application of benzol, in lieu of petroleum spirit, as a detergent, in the *Bull. Soc. Ind. Mulhouse.* He states it as an advantage of benzol over petroleum benzin that it is not electrically excitable, but as a drawback that it is injurious to the health of the workmen.

According to Russig (*Chemische Zeitschrift*, iii., p. 780), in France large quantities of solvent-naphtha, boiling from 90° to 160°, are used as detergents in lieu of petroleum spirit, which is weighted by a high duty.

Benzol is largely used for extracting fat from bones and seeds, where it does one and a half times the service of petroleum spirit, but in the extraction of seeds it has the drawback of taking up too much colouring matter at the same time.

Fr. Frank (*Chem. Ind.*, 1901, p. 266) found that benzol dissolved from dry bones within an hour 9 per cent. fat, while petroleum benzin in the same apparatus and during the same time took up only 6 per cent. This is confirmed by Mennicke (*Chem. Zeit.*, 1900, pp. 917 and 923).

In the manufacture of *lac-varnishes*, technical benzol is employed both as a solvent for cheap iron lacs, and as an addition to spirit-lacs which thereby acquire a greater value in several respects. More particularly the quality, which yields 90 per cent. on boiling up to 175°, has found employment for the preparation of very fine lac-varnishes, in lieu of oil of turpentine. For this purpose it must be well washed, and possess no disagreeable smell. It is also used for photographic purposes.

According to Guttmann, Herzfeld, and Beer (Ger. P. 101414) the solvent-power of 90 per cent. spirit of wine for *petroleum* can be raised by 12 to 20 per cent. by the addition of 8 to 10 per cent. benzol. By adding, in addition to that, 4 per cent. of naphthalene, the solvent-power can be raised to 23 to 24 per cent.

Duran (Ger. P. 289205) employs benzol as a solvent in the manufacture of briquettes (patent fuel).

Benzol also dissolves very easily *alkaloids*, *rosins*, and *asphalte*, and is therefore employed for extracting or purifying these matters. Its application for pickling timber has been mentioned *supra* (by the process of Krojanker), p. 689.

Benzenoid hydrocarbons have turned out to be eminently suitable as solvents for the *removal of the naphthalene contained in coal-gas*, which causes very awkward obtrusions in the service-pipes, as first proposed by Bunte and Eitner (*Chem. Zeit.*, 1899, Rep. pp. 53 and 216; *supra*, p. 823), and recommended by Breitkopf (*J. Gasbeleucht.*, 1899, p. 671). According to Schäfer (*Einrichtung und Betrieb eines Gaswerks*, pp. 403 *et seq.*), the most suitable oils are commercial benzol No. IV. (crude xylol), or the two solvent naphthas, I. and II., which have a prominent solvent-power for naphthalene and distil over between 125° and 180°. This process consists in embodying with the coal-gas the vapours of such hydrocarbons which condense at the same temperature as naphthalene, and at the same time possess a strong solvent-power for it. The crude xylol should be condensed again for the most part when the gas cools down; it should not contain any more volatile substances which would carburate the gas and cause trouble by the deposition of soot on the glowing substances. According to Schäfer, the addition of xylol vapour is made before the cooling of the gas by means of an apparatus of just the same construction as those used for carburetting the gas by means of benzol (see below, p. 1021). The quantity of xylols required is 20 g. per cubic metre of gas, 100 g. crude xylol; dissolve 21 g. naphthalene at 0°. The xylol, *plus* the dissolved naphthalene, condenses in the nearest hydraulic pot, and can be recovered by distillation. For the just-described process, the Deutsche Continental Gas-Gesellschaft, of Dessau, has constructed an apparatus mounted on wheels; and so have Wahl-Güstrow (*J. Gasbeleucht.*, 1901, p. 533), and Lübke (Ger. P. 217089, of 1907).

Use of Benzol for Denaturing Spirits.—Benzol is to some extent soluble in spirit of wine of 86 volume per cent., and has hence been proposed for denaturing spirit, especially for the manufacture of varnishes. On diluting with water, most of the benzol separates, but the spirit retains its smell and taste. According to Kraemer, an addition of 0·1 per cent. pyridine bases is advantageous. In Switzerland solvent-naphtha is used for this purpose (Lunge, *Z. angew. Chem.*, 1890, pp. 71 and 262). *Cf.* also the patent of Herzfeld and Beer (p. 1014). This process has been adopted in several countries.

According to tests made in the Technische Reichsanstalt (*Mitt.*, 1886, p. 11) equal volumes of yellow heavy naphtha (sp. gr. at 15° 0·887, boiling from 163° to 195°) and 90 per cent. alcohol yield a milky liquid, keeping most of the oil in solution and not becoming clear even on adding a great quantity of absolute alcohol. On fractionating the mixture, it was shown that the solubility in alcohol decreases with the rise of the boiling-points.

Kraemer (*Chem. Ind.*, 1899, p. 31) contends that a mixture of equal portions of petroleum and 90 per cent. benzol, which dissolves even in 94 per cent. alcohol in all proportions, should be permitted to serve as denaturing agent under the usual precautions against abuse. Not less than 10 per cent. of this agent should be added to the spirit, which would prevent its being used for illegal purposes, and it would be the cheapest possible agent for denaturing.

A decree of the German Imperial Governments of 8th August 1899, prescribed for the denaturation of spirits, an addition of 2 per cent. benzol, 1 per cent. methyl alcohol, and ¼ per cent. pyridine bases. The benzol used for this purpose should fulfil the following conditions:—Ten c.c. of benzol is shaken in a cylinder divided in tenths of a cubic centimetre with 10 c.c. of water. After five minutes the upper layer (of benzol) should occupy at least 9·9 c.c. On distilling 100 c.c. benzol in the way prescribed for wood-spirits, no more than 1 c.c. should pass over up to 80°, and up to 100° no more than 94 per cent. and no less than 96 per cent. If the barometer during the distillation is not at 760 mm., 0·45° should be added to the just-named temperatures for every 10 mm. above 760 mm., or deducted for every 10 mm. below the temperatures. If 5 c.c. of the benzol is shaken up in a stoppered bottle with 5 c.c. pure concentrated sulphuric acid during five minutes, and then allowed to rest, the colour of the lower stratum after two minutes' rest should not be darker than that of a solution of 0·5 g. pure potassium bichromate in 1 litre of 50 per cent. sulphuric acid. The smell of the alcohol denatured in this way is less disagreeable than that prepared in the old way, and it is superior to this for lighting and polishing, but when burned in unsuitable burners it yields a little soot. Renaturation is not possible.

A new rule (of Oct. 1902) allows to employ only half of the otherwise necessary proportion of denaturing mixture of pyridine bases (*cf.* p. 903), if to 100 litres of alcohol 2 to 20 litres of benzol is added together with ¼ litre of a solution of crystal violet. The benzol used for this purpose, on distillation, should not yield more than 1 per cent. at 77° and not less than 90 per cent. at 100°. The smell of spirits denatured in this way is less unpleasant than that denatured in the old fashion, and it is better adapted for lighting and polishing purposes, but it burns with a rather sooty flame when using imperfect lamps.

According to the "Vierteljahrshefte zur Statistik des Deutschen Reichs," the following quantities of benzol (sp. gr. 0·88) have been used in Germany for denaturing spirit of wine: 129,332 litres (114 tons) in 1909; 124,070 litres (109 tons) in 1910; 129,297 litres (113·75 tons) in 1911.

Use of Benzols for Illuminating Purposes.

This use dates back to the first times of distilling coal-tar, and it has in recent years made very important progress. It extends in two directions, viz., in the employment of benzols, especially those boiling at higher temperatures, as a direct illuminant, and in that of employing the more volatile fractions for improving the illuminative power of other liquid or gaseous substances.

(a) *Direct Use as Illuminant.*—The highest-boiling oils obtained by the steam rectification, if they cannot be worked in with solvent-naphtha, are sold as *burning-naphtha.* Coal-tar naphtha, whether pure or mixed with petroleum spirit, is not adapted for burning in ordinary lamps or at all in closed rooms, but merely for special lamps, without wick or chimney, which burn well even in strong wind and rain, and hence serve for lighting factories, courtyards, booths at fairs, etc., in lieu of gas. Good naphtha, no doubt, gives a very fine white light. Figs. 223 and 224 show a suitable lamp for this purpose (Halliday's patent). Fig. 223 is the lamp itself, on a scale of 1 : 12; Fig. 224, the burner, on a scale of 1 : 2. *a* is the reservoir for naphtha, from which a thin tube *b* leads downwards; the cock *c* regulates the outflow; the tube *b* is almost entirely filled up by a round wick which extends nearly to the burner, and the sole purpose of which is to make the outflow of the naphtha gradual. The hook *d* serves for hanging up the lamp. In the burner we notice the lateral tube *e*, communicating with *b*, and introducing the naphtha. This flows downwards in the narrow channel *f*, which is closed by the thin screw *g*, the channel *h* being closed by *i*. The naphtha must rise from *h* in the fine central channel, leading to a hole, *k*, across the burner. Here it would run off if the burner had not been previously heated sufficiently to evaporate it at once. The vapour mixed with the air entering at *k* rises in the central channel *l*, issues through the holes in the burner-head, and, on being lighted, produces a star-shaped flame. The draught generated by this suffices for preventing the naphtha-vapour from issuing into the open air instead of into the channel *l*. The screw *n* permits regulating the orifice of the fine channel

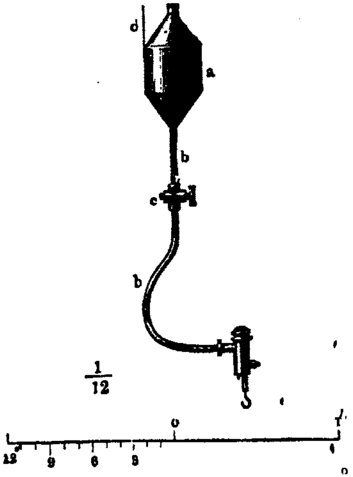


FIG. 223.

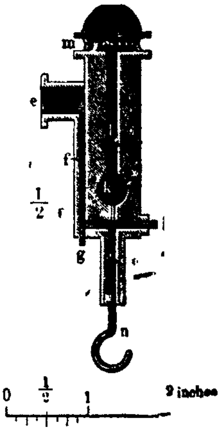


FIG. 224.

between *h* and *k*. Here also a small cup may be fixed for some naphtha to be lighted in order to effect the first heating of the burner, the tap *c* being then closed. Otherwise the burner-head is put into a fire till it is warm enough. When this is the case, the tap *c* is opened, the vapour issuing out of the holes *m* is lighted, and the size of the flame regulated by *c*. Once lighted, the burner always remains warm enough.

When burning-naphtha can be sold in quantity, it is advisable to mix it with *petroleum spirit*, which in this case is an improvement, and especially tends to keep it colourless. The petroleum spirit can be pumped into the still after the solvent naphtha has come over, and can be distilled along with the burning-naphtha. Care should be taken that about equal parts of coal-naphtha and petroleum-spirit distil together; the smell of the latter will then be imperceptible. Or else the petroleum spirit is mixed with the naphtha after distillation. The best descriptions of petroleum-spirit for this purpose are those which give off very little below 100°, but nearly the whole up to 170°.

Since the recovery of benzol from coke-oven gases has immensely increased the available quantity of this article, it is of course a most momentous question for the tar-distillers to find fresh outlets for it; and there are prospects for employing benzol as an illuminant, to replace petroleum at least partially. Kraemer (*Chem. Ind.*, 1899, p. 32) finds that a mixture of 3 parts benzol, 4 petroleum, and 6 96 per cent. spirit of wine answers very well for *incandescent lamps*. The mixture has the same illuminating-power as petroleum itself, but 20 per cent. more is consumed of it than of pure petroleum. Russian petroleum serves even better than American for this mixture, which at the present prices of benzol and spirit would already pay, but would be more remunerative if the price of petroleum were to be raised to any considerable extent. The mixture proposed by Kraemer (*Mitt. Gewerbefleiss*, 1897, p. 90) solidifies only at −17°; by a consumption of 58 to 61 g. it gives a light equal to 17 to 19 standard candles when used in an ordinary flat burner. *Cf.* also Hönigsberger (*Z. angew. Chem.*, 1909, p. 672).

Beyling (*Glückauf*, 3rd Feb. 1915) employs for miners' lamps a mixture of 25 parts purified 90 per cent. benzol with 75 parts 95 per cent. spirit (alcohol). If less than 25 parts benzol is used, the lighting-power is not sufficient; more than 25 parts does not essentially improve it, and at 30 parts the formation of soot and the incrustation of the lamp-wick are very awkward. The illuminating-power of this mixture is about three-fourths of that of the ordinary petroleum spirit; its behaviour in the presence of fire-damp is just the same, or rather better. The benzol lamp is already in use in a number of coal-pits. The lamps must be cleaned after every shift.

According to Frank (*J. Gasbeleucht.*, 1902, pp. 9 *et seq.*) a mixture of 47 volumes of "technical benzol" (consisting of about 95 benzene + 5 toluene, and yielding at least 90 per cent. up to 90° C.) with 15 volumes solvent naphtha (yielding 90 per cent. up to 175°) and 38 volumes spirit of wine (94 per cent.) which solidifies only at −17° C., is very well adapted for street lamps. If burnt in an ordinary flat burner, 50 to 61 g. per hour are required for an illuminating power of 17 to 19 candles per hour.

"Carbosprit" is a mixture of 40 spirit of wine with 60 benzol, employed for incandescent lamps by W. v. Crobloch (*J. Gasbeleucht.*, 1902, p. 194).

Plehn (Ger. P. 156988) makes an illuminating liquid from 70 to 95 volumes of 90 per cent. spirit of wine + 5 to 30 volumes of purified "solvent-naphtha," boiling between 160° to 180° C. This mixture burns in an ordinary lamp, provided with a wick without any coat, and is to be used in the place of petroleum.

The firm Denayrouze has constructed an elegant benzol lamp for use in dwelling-rooms, equal to any lamp for petroleum spirit. It is stated that 5 g. of the benzol, called "lusol" by that firm, suffices for 1 candle-hour.

Benzol is also used as an addition to "solidified spirit of wine" for heating and lighting purposes (*Pharm. Zeit.*, 1902, p. 318).

W. van der Heyden (Ger. P. 176366) *solidifies* benzol (as well as petroleum or petroleum benzin) by mixing it with glue, made into a jelly or dissolved in water, and drying or hardening the glue by formaldehyde.

The benzol lamp of Fernholz is supplied by the Fernholz-Licht-Gesellschaft at Schenkendorf-Königswusterhausen for lighting up to 3000 candle powers. The benzol is gasified at an air-pressure of 2 or 3 atmospheres, either at a central station or separately for each lamp. Pure toluene (which has the advantage of resisting solidification in cold weather) can be used for it without any difficulty (Schreiber, *Kokerei-*

industrie Niederschlesiens, 1911, p. 48). In a Fernholz apparatus of 1500 candle power, mounted in a factory yard, benzol is submitted in a 30-litre vessel to a pressure of 2 to 3 atmospheres by means of a hand-pump, and this mixture of air and benzol is supplied through a flexible copper tube to a lamp, placed high up, where it issues through a small orifice into the suspended burner, and at the same time aspirates the air for combustion, heated outside. By the thus produced high temperature a suspended glow-cylinder (Glühstrumpt) which is protected by a bell-jar against the outside weather, is made to give out a strong light. The burner can be regulated from below. For 1500 candle power it consumes per hour 0·4 kg. benzol. These lamps, which are especially adapted for lighting factory yards, workshops, railway stations, etc., are supplied for outside lighting at the price of £8, for inside lighting at £2 to £4 per lamp.

Recently the Autogen Werke für autogene Schweissmethoden sells a suspended benzol lamp by the name of "Oxybenz-Lampe," which is claimed to have certain advantages against the Fernholz Lamp. It consumes for 100 Hefner candles from 180 to 200 g. benzol per hour.

(b) *Carburetting Gas by Tar-oils.*—Of much greater importance than the direct use of benzol for lighting purposes is the use of tar-oils for increasing the illuminating-power of ordinary coal-gas, by what has been styled "carburetting." Almost from the beginning of the coal-gas industry, inventors have been engaged in discovering a means of enriching it, by mixing it with the vapours of substances possessing a higher illuminating-power.

A number of years ago the illuminating-power of gas was its only standard of value; the carburation of gas then played a very great part, and consumed large quantities of benzol, which is most easily employed for this purpose. But since the enormous progress made by incandescent light (Welsbach mantles and their imitations), the carburation by benzol is less important. Water-gas, which is not an illuminant at all, gives per heat-unit a much higher efficiency with a Welsbach mantle than ordinary coal-gas, and this again a higher efficiency than oil-gas (priv. comm. by Dr Bueb).

The subject of carburetting gas has been extensively treated by Letheby,[1] Solomons,[2] Bunte,[3] Ries,[4] Stenhouse,[5] Irwin,[6] Bueb,[7] and Rau.[8] We must refer the reader to these papers, and to those which have appeared afterwards in such numbers that we must abstain from going further into them.

Dr Letheby's specification, which was adopted by the London lighting authorities (p. 918), must yield a product essentially consisting of xylene. He did not assume this to act better than benzene or toluene; but he selected that product because it was at that time not employed at colour-works, and consequently was lower in price. By Knublauch's investigations (*Berl. Ber.*, 1881, p. 240) it has been ascertained that, in fact, benzene, for equal weights, imparts the greatest illuminating-power to gas, and that the higher homologues act only in proportion to their molecules, only the carbon of the benzene nucleus being set free in a luminous form, whilst that of the methyl groups is burned directly to carbon dioxide. Formerly it seemed out of the question to employ benzene itself for carburetting either coal-gas or air (although the first person who manufactured benzene on an industrial scale, Mansfield, had the latter object in view), as the high value of benzene was an impediment to such an employment; but at the recent prices, benzene is quite cheap enough for this purpose.

It is well known that gas, when being passed in a continuous stream through a liquid containing several volatile substances of different boiling-points, will in the first instance carry away a larger quantity of the more volatile portions, and that the composition of the remaining liquid must consequently undergo constant changes. This is a drawback to all carburetting liquids, but much less to a liquid approaching pure benzene, such as commercial 90 per cent. benzol, as they are all such compound substances. Thus carburetting naphtha made according to Letheby's specification, in experiments made by G. E. Davis (*J. Soc. Chem. Ind.*, 1886, p. 4) yielded at first 5·25 gall. of the lighter oils to 10,000 cub. ft. of gas, but after a time scarcely anything was vaporized, and the boiling-points of the remaining naphtha were much higher. Exactly the same thing occurred with 50/90 per cent. benzol, and even with 90 per cent. benzol (which under similar circumstances yielded about 15 gall. to 10,000 cub. ft. of gas). The same happens with gasoline and other mixtures of fatty hydrocarbons. The irregular evaporation of the fluid is a serious drawback in the case of all mixed liquids, but it would not apply to a uniform substance like naphthalene. Davis found that the residual fluids contained in absolute quantities more of the higher-boiling hydrocarbons than originally; evidently the gas took up the benzene by preference, and deposited its own hydrocarbons of lower vapour-tension in the carburetting-fluid, thus making it still more unsuited for enriching the gas.

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[1] *Chem. News*, xi., p. 276.

[2] *J. Gasbeleucht.*, 1892, p. 5.

[3] *Ibid.*, 1893, p. 442.

[4] *Ibid.*, 1894, p. 1.

[5] *J. Soc. Chem. Ind.*, 1895, p. 435.

[6] *Ibid.*, 1895, p. 546.

[7] *Z. angew. Chem.*, 1895, p. 622.

[8] *Die Aufbesserung des Leuchtgases mit Benzol*, 3rd ed. (Kattowitz, 1895).

The carburation takes place either at the burner itself or at the gas-works. In the former case it is troublesome to constantly replenish the reservoirs with the carburetting-liquid. There is rather less trouble in this respect, but more in others, in the case of naphthalene, as described, p. 847. The apparently easier plan of carburetting at the gas-works involves the necessity of so treating the mixture that the gas may not deposit the carburetting-substances on its way through the network of pipes. The American water gas-works therefore "*fix*" the carbon of the hydrocarbon vapours mixed with the water-gas by passing the mixture through red-hot retorts, or in some similar manner. In this process, no doubt pyrogenetic changes are effected similar to those described, pp. 185 *et seq.* When carburetting gas with low-boiling benzol, such "fixing" is not necessary; the methane present in the gas seems to render the benzene-vapour more stable as such.

The quantity of benzol required for carburetting coal-gas differs from 2 to 4 g. per hour and candle. The "mixed gas," recently very much in use, consisting of $\frac{2}{3}$ water-gas + $\frac{3}{8}$ coal-gas, requires the addition of 40 g. benzol per cubic metre to attain a power of 16 candles. Sospicio states the quantity required for a mixture of $\frac{1}{5}$ water-gas + $\frac{4}{5}$ coal-gas = 23 g. for 16 candles (see below).

It has been asserted that benzol, when applied to carburetting gas, destroys the dry gas-meters. This is contradicted by Witzek (*J. Gasbeleucht.*, 1904, p. 656) and by Messerschmidt (*J. Gasbeleucht.*, 1906, p. 235).

Carburetting Water-gas.—Much more important than for ordinary coal-gas is the carburetting process for *water-gas*, which is now made at all important gas-works, in order to be mixed with coal-gas. We always understand by the term "coal-gas" that made in the old way in gas-retorts. The water-gas, also called "blue gas," has no illuminating-power, and its heating value is only 2900 metrical heat units, against 5000 heat units in the case of ordinary coal-gas. Mixing the latter with a large proportion of water-gas would therefore decidedly reduce its value, both in respect of for heating and power, and in that of its application for incandescent lighting, where it is also in the first line a question of the heating-value of the gas. This can be remedied by carburetting the blue gas, before mixing it with coal-gas, either in the cold by means of benzol, or at a higher temperature by the products of decomposing mineral oils.

Nowadays, therefore, benzol is principally used at gas-works for carburetting "blue" water-gas, or its mixture with coal-gas. A great many apparatus have been constructed for this purpose, mostly on the same principle as gas-scrubbers, but differing from these by being heatable. We cannot in this place enumerate all those apparatus, but it may be suitable to describe one of the best of them, the "Munich carburetter" of the Berlin-Anhaltische Maschinenbau-Aktiengesellschaft, shown in Fig. 225. It consists of the evaporator, A, the store-vessel, B, provided with a filling-arrangement and an index, the regulator for supplying the benzol and the connecting-pipes. The evaporator A is a rectangular cast-iron box, containing corrugated heating elements, covered with coarse linen cloth. The benzol runs through the regulator *r* and the pipes b_3 and b_4 on to the cloth, which soaks it up and divides it evenly over the whole evaporating-surface. The gas enters at G, flows over the plates and leaves the apparatus at G, in the carburetted state. The testing-cock b_5 allows of ascertaining whether the benzol is being completely evaporated, and not collecting at the bottom of A.—The store-tank, B, holding 500 litres benzol, is constructed on the principle of a Mariotte bottle, so as to cause its contents to run out in an even stream, independently of the height of the liquid. B is completely closed, provided with a false bottom, and its bottom part N is connected by pipe *g* with the gas-main, so that its inside is not in contact with air, which precaution

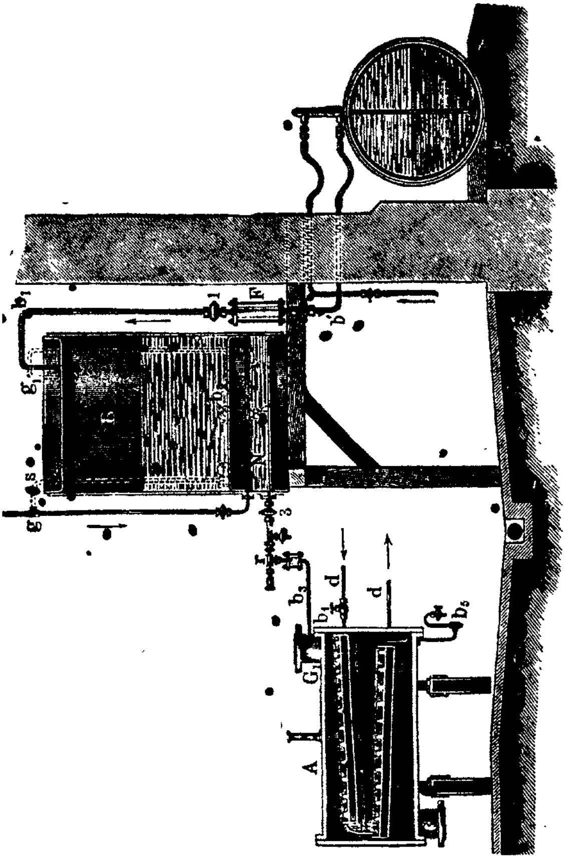


FIG. 225.

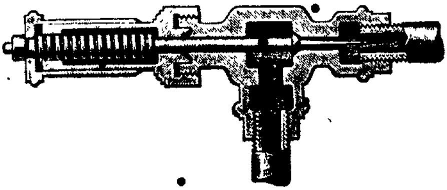


FIG. 226.

is very important in respect of the danger of fire. On opening tap 3, benzol flows out; but before the level of the liquid in N can go down, gas enters through pipe g into the tank B, with the effect that benzol flows out of g_2, and tap 2 only until the rising level of N shuts off again tap g_1. The outflow of benzol is therefore always under the pressure of the constant height of the liquid in N. In order to fill tank B, tap 2 is closed, and a double pipe is fixed on the bung-hole of a benzol cask, which is connected on one side with a high-pressure water conduit, and on the other side with the supply-pipe b_1. The water then displaces the benzol and forces it through tap 1 into tank B, the gaseous contents of which escape through s and g into the gas main.

The supply-regulator, shown separately in Fig. 226, contains a spindle with a parabolically shaped point, 40 mm. long, moved backwards and forwards by means of a millimetre-screw. Together with the spindle, an envelope provided with a circular division moves on a cylinder with millimetre marks. For every supply-regulator a table is sent along, by means of which the desired rate of the supply of benzol can be regulated.

According to a report of the Committee of American gas-engineers (*J. Gas Lighting*, 1910, p. 239; *J. Soc. Chem. Ind.*, 1910, p. 202), the carburetting of gas by benzol increases its illuminating power, but hardly at all its heating value, and is therefore not to be recommended for water-gas. They consider it useless to enrich a gas, saturated with light hydrocarbons, by benzol, because in this case the light hydrocarbons will to a great extent separate during the passage of the gas through the service pipes. Hence they recommend first removing part of the hydrocarbon vapours of low vapour tension by compressing, cooling, or washing the gas with an absorbing oil.

Benzol is also used, like petroleum spirit, for preparing carburetted air, known by the designation *Aërogen gas* or *Benoid gas*. This can be affected by the well-known apparatus used for petroleum spirit or gasolin, but special apparatus for this purpose have also been proposed, *e.g.*, in the French patent of Léotard and Diguet.

The *valuation of tar-oils for the process of carburetting water-gas, etc.*, is treated by Spiegel (*J. Gasbeleucht.*, 1907, p. 45; *J. Gas Lighting, Water Supply, etc.*, 1907, p. 822). The ordinary tests do not indicate their value for that purpose, nor does the calorific test, since oils which are not sufficiently volatile to be taken up by cold gas are useless in this case, and so is naphthalene. Hence, many gas engineers trust only to practical trials on a large scale. Spiegel asserts that an oil is all the more valuable as carburetter the more nearly saturated its hydrocarbons are. He therefore determines the proportion of hydrogen in it by the ordinary process of ultimate elementary analysis. He describes a way of calculating from this the carburetting value of the oils, but since he confines this to the heavy oils used for carburetting water-gas by the hot process, not to those which are employed in the cold, and since he himself admits that further experiments are necessary for comparing his data with the results obtained on the large scale, we must refer the reader to the original.

Use of Benzol and its Congeners for driving Motors and Motor-cars.

The employment of benzol for these purposes, in lieu of petroleum spirit or spirit of wine, although of quite recent date, promises to be one of the most important outlets for this product. It is indeed stated (*e.g.* by Köhler) that at the present time much more benzol is sold for motoric purposes than for the manufacture of aniline colours. It is in this respect a most serious competitor with petroleum spirit (benzin), and a practically unlimited field seems to be open for it in that direction. The extent of this field may be judged from the following figures, given by Rau (in Lunge and Koehler, p. 950). Almost entirely through its application for motor-cars, the consumption of petroleum spirit in Germany has increased from 30,000 tons in 1892 to 115,000 tons in 1908. In that year there was 400,000 tons of petroleum spirit sold in Europe, 800,000 tons in North America.

The first attempts at replacing petroleum spirit or spirit of wine by benzol failed, because it was not handled in the proper way, also because regard had not been had of the solidification of benzol a few degrees below 0°. A great mistake was also committed by employing *crude* benzol, which leaves an evaporation residue of 0·2 to 2·3 g., increasing up to 5·4 g. when stored for three months, which residue stops up the machinery;

whereas purified 90 per cent. benzol leaves no residue, but has even to a greater extent the awkward property of freezing. This drawback has been remedied by appropriate additions. The Paris Automnibus Company mixes the benzol with the same volume of spirit of wine. O. Mohr (Ger. P. 216699) prescribes mixtures of benzol, benzin, and spirit of wine, which at −25° do not separate any solid matters and completely distil between 42° to 78°. The same effect is produced by the addition of the non-freezing higher homologues of benzol. Thus, for instance, the *ergin* of the Rütgerswerke-Aktiengesellschaft, which is specially intended for driving stationary motors, consists of a purified mixture of benzol with its higher homologues, up to tetramethylbenzenes, in the same proportion as they occur in coal-tar. The *autin* of the Gewerkschaft Deutscher Kaiser is a mixture of benzene and toluene, not freezing at −17°.

In Paris now most omnibuses are driven by benzol motors. Even in the pits and chemical works of the coal-districts many locomotives are worked by benzol, and such are now also introduced on the Prussian State Railways. The progress made in Germany in that direction is best proved by the following figures:—In 1901 the benzol used for motor-driving amounted to 300 tons; in 1907 to 3000 to 4000 tons; in 1910 the Deutsche Benzolvereinigung alone sold 31,332 tons of motor-benzol.

British patents: Franke (18225, 1914); Higgins and Preston (23876, 1914).

A great many statements on this matter have been made by Neumann (*Die Verbrennungskraftmaschinen*, 1906, p. 304); Warschauer (*Z. angew. Chem.*, 1908, p. 1537); Hönigsberger (*ibid.*, 1909, p. 671); Lehmbeck (*Automobil-Zeitung*, 1908, No. 52); Terres (*J. Gasbeleucht.*, 1914, lvii., pp. 893, 907, 917, 929); in *J. Ind. Eng. Chem.*, 1914, vi., p. 239; 1915, vii., p. 73; by Watson, Froth, and others (*J. Soc. Chem. Ind*, 1915, p. 266), by Dieterich (*Pharm. Post*, 1914).

Various Other Uses of Benzol.

Manufacture of Lampblack from Benzol.—Kraemer many years ago pointed out that benzol, at the low prices obtainable for it in various circumstances, might be advantageously employed for the manufacture of *soot*, technically called *lampblack*. This suggestion was followed up in several patents of Thalwitzer (Ger. Ps. 109826 and 119830, of 1899). He obtained lampblack of excellent quality from a mixture of benzol with combustible gases, prepared in such a way that it contains about as much carbon as good oil-gas. Or else he employs air, or hot combustible gases, saturated with benzol vapour, but in such a way that the mixture is not inflammable. This process might be important in the manufacture of coke by distillation of coal, or other similar industries.

Use as a Disinfectant, Sterilizer, Insect-killer, etc.—A germicide disinfectant is prepared by Weyl (Ger. P. 135898) by passing gases containing ozone into benzol, heated to 60° to 70° C. This patent lapsed very soon.

The action of benzol and other hydrocarbons on microbes has been examined by Berthelot (*Comptes rend.*, cxxxvii., p. 953) and Staehelin (*Chem. Zentr.*, 1904, i., 1024).

Nobbe and Richter (*Chem. Zentr.*, 1905, i., 116) employ benzol for sterilizing the soil, in order to obtain high crops of corn.

Xylol and cumol are employed for sterilizing catgut at 160° C. (Merck's *Jahresber.* for 1901). Beslier (*Chem. Zentr.*, 1905, ii., 69) employs benzol for the same purpose.

Wolff (*Pharm. Zeit.*, 1902, p. 610) recommends benzol as the best agent against *lice* of all sorts.

For these purposes benzol is sometimes used in the shape of a mixture with soft soap.

Employment of Benzol for soldering and cutting of Metals.—Up to recent times, the production of high temperatures in the working of metals has been brought about by the oxyhydrogen flame. An improvement on this is the flame produced by a mixture of oxygen and acetylene. A further improvement is supposed to be the substitution of benzol for acetylene, which, it is asserted, produces the same effect at a mere fraction of the cost. Apparatus for this purpose is supplied by the "Autogen-Werke" für autogene Schweissmethoden, of Berlin.

Sydney Young (*Proc. Chem. Soc.*, xviii., p. 104; *Chem. Zentr.*, 1902, i., 1317) makes *absolute alcohol* by several times fractionating a mixture of spirit of wine with benzol. The traces of benzol remaining in the alcohol are to be removed by a special process, hardly fit for technical use. This process is the subject of Ger. P. 142502.

Darmstaedter (Ger. P. 125404) employs toluol to form an emulsion in order to obtain smooth precipitates in *electrolytic baths.*

Of *safety-explosives* manufactured from nitroderivatives of benzol hydrocarbons we mention *Bellite* (nitro- and dinitro-toluol); *Fördite* (nitrotoluol); *Nigro-powder* (trinitrotoluene); *Roburite* (dinitrobenzol); *Trotyle* (trinitrotoluene); *Vigorite* (nitrated hydrocarbons).

Statistics.

The productive capacity of the United Kingdom for benzol of various types was estimated by Levinstein (*J. Soc. Chem. Ind.*, 1886, p. 351) for the year 1886 at nearly 3 million gallons, of which quantity Germany took 1½ millions (in addition to ½ million home production), England ½ million, France and other countries the remainder.

Germany, during the years 1870 to 1880, produced only about 1200 tons per annum; 1890, already about 4000 to 5000 tons; 1896, 7000 tons; 1901, 25,000 to 30,000 tons; 1904, 36,000 to 38,000 tons. In 1906 the Rhenish-Westphalian provinces alone produced nearly 40,000 tons of benzols, so that the German colour-works, which formerly had to get about seven-eighths of the benzol they required from Great Britain, now get it nearly all in Germany. If all the coke in that country was made by recovery-ovens, she would produce upwards of 70,000 tons, which is far above the quantity saleable at present or in the near future. Indeed, during the last few years a good many new coke-ovens have been built in Germany on the old plan, as there was not enough chance for selling the products made by recovery-ovens.

Compare also the statements on the production of benzol in various countries, *supra*, p. 156.

Russig, in his various reports on coal-tar products in the *Chemische Zeitschrift*, gives the following statistics for the importation and exportation from Germany (the figures denote metrical tons, at 1000 kg.) in the years from 1899 to 1905:—

Imported.

Year	1899.	1900.	1901.	1902.	1903.	1904.	1905.
Sulphate of ammonia	28,808	23,105	44,407	42,251	35,168	35,165	48,005
Gas-liquor	21,504	26,407	13,765	10,267	(?)	(?)	(?)
Anthracene	4,305	3,894	3,296	2,876	2,048	1,230	1,350
Carbolic acid and other phenols	3,908	4,225	4,538	5,154	5,016	5,266	5,536
Naphthalene	3,776	9,802	12,596	11,464	14,481	12,444	11,645
Coal-tar oils, light	5,291	7,210	7,723	7,591	8,063	5,779	8,104
Coal-tar oils, heavy	2,543	3,286	9,267	6,800	6,579	5,608	7,265
Tar of all descriptions	39,696	35,953	37,508	40,574	36,788	40,641	37,292
Pitch, asphalt, wood-cement[1]	61,534	80,765	62,299	88,536	94,377	85,049	82,461

Exported.

Year	1899.	1900.	1901.	1902.	1903.	1904.	1905.
Sulphate of ammonia	1,553	2,431	9,842	5,744	5,592	10,696	27,589
Gas-liquor	16,971	17,068	15,400	15,857	(?)	(?)	(?)
Anthracene	...	...	1	154	1	49	13
Carbolic acid and other phenols	2,850	2,452	3,198	3,357	3,102	3,898	5,275
Naphthalene	1,270	1,274	1,261	2,455	2,[illegible]83	2,878	2,735
Coal-tar oils, light	2,755	2,994	2,260	2,222	2,982	4,390	6,560
Coal-tar oils, heavy	8,640	10,506	5,992	5,704	8,596	12,982	23,292
Tar of all descriptions	30,678	32,437	31,433	29,818	31,898	32,872	42,889
Pitch, asphalt, wood-cement[1]	37,771	36,921	39,670	40,595	49,785	55,359	62,640

In the year 1906 a new tariff and new designations were introduced in the German Customs Union, and for this year no useful statements can be made. For 1907 the following figures can be given for the importation and exportation into and from Germany:—

	Imported. Tons.	Exported. Tons.
Coal-tar	29,276	32,062
Coal-tar pitch	20,283	16,892
Benzol (from coal-tar)	4,114	1,681
Toluol, cumol, and other light coal-tar hydrocarbons	5,683	3,394
Heavy coal-tar oils and asphalt-naphtha	7,034	50,802
Naphthalene	10,144	5,980
Anthracene	2,418	32
Phenol, crude and pure	5,277	3,561
Cresol	3	410
Sulphate of Ammonia	33,522	57,493

---

[1] How much of this is coal-tar pitch cannot be ascertained.

Beginning with the year 1907, the German Official Statistics give separate figures (1st) for "benzol" and (2nd) for "toluol, xylol, cumol, other light coal-tar oils, and hydrocarbons from oil-gas making." These are:—

Year.	Benzol.		Toluol, xylol, cumol, etc.	
	Importation.	Exportation.	Importation.	Exportation.
1907 . . .	4115·1 tons	1680·8 tons	5683·1 tons	3999·4 tons
1908 . . .	4254·7 ,,	998·5 ,,	3366·9 ,,	5207·8 ,,
1909 . . .	3194·6 ,,	1808·2 ,,	3394·2 ,,	7236·9 ,,
1909, value .	511,000 marks	248,000 marks	882,000 marks	1,327,000 marks
1910 . . .	2538·5 tons	12757·7 tons	5382·7 tons	9772·4 tons
1910, value .	406,000 marks	1,675,000 marks	1,400,000 marks	1,481,000 marks
1911 . . .	2,371 tons	21,996 tons	5,052 tons	4,997 tons

Fluctuations in the Prices of Benzol.

For the *English* market the following diagram, Fig. 227, by Kraemer, shows the fluctuations of the prices of benzol during

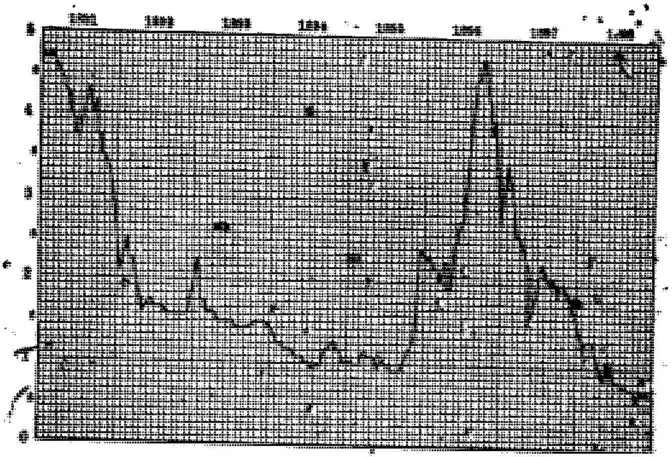


FIG. 227.

the years 1891 to 1898, the perpendicular lines indicating the shillings and pence per gallon.

The diagram, Fig. 228, shows the English prices (expressed in marks per 100 kg.) from 1899 to 1909.

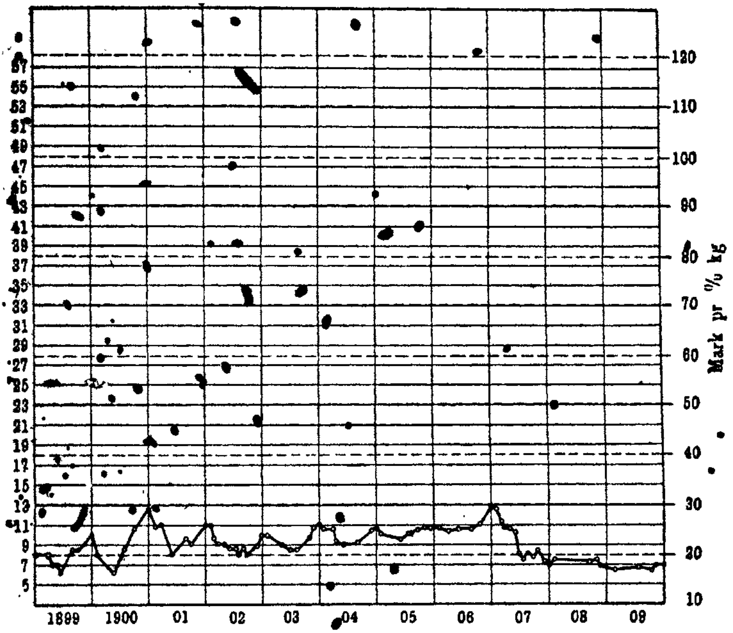


FIG. 228.

From the figures given on p. 1032 it appears that, whereas in former years the requirements of Germany in the matter of benzol had to be to a great extent covered by importation (chiefly from England and Belgium), that country since 1909 has become an exporter of those hydrocarbons, so that the quantity of benzol exported now vastly exceeds the importations. This is due to the enormous development of the recovery of the by-products in the manufacture of coke—a development which has created an over-production of benzol, finding its expression in the great changes of the market values of this article. We here quote first the statements made by Frank (*Chem. Ind.*, 1901, p. 238) for the years 1882 to 1901 as to the price of 90 per cent. trade benzol:—

In 1882	between	175	and	400	marks per	100 kg.
„ 1885	„	50	„	90	„	„
„ 1890	„	100	„	125	„	„
„ 1892	„	40	„	60	„	„
„ 1895	„	25	„	60	„	„
„ 1896	„	50	„	120	„	„
„ 1897	on the average			65	„	„
„ 1899	„		„	25	„	„
„ 1899 „ 1900	„		„	20	„	„
„ 1901	„		„	30	„	„

The *Jahrbuch für den Oberbergamtsbezirk Dortmund*, 1910, p. 711, makes the following statements as to price of benzol per ton (1000 kg.):—

In 1899 . .	169·50 marks	In 1905 . .	215 marks
„ 1900 . .	178 „	„ 1906 . .	191·80 „
„ 1901 . .	197·50 „	„ 1907 . .	170 „
„ 1902 . .	210 „	„ 1908 . .	170 „
„ 1903 . .	210·30 „	„ 1909 . .	158·90 „
„ 1904 . .	211·50 „		

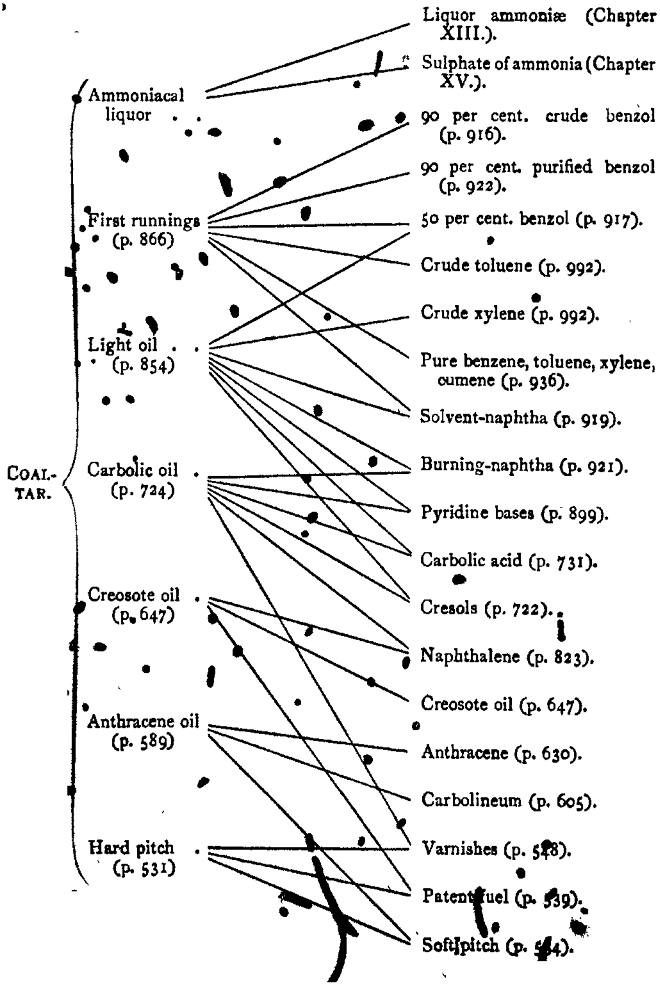
The Deutsche Benzolvereinigung quotes the following average prices in marks per 100 kg.:—

Year.	90 per cent. benzol.	Pure benzene.	Pure toluene.	Pure xylene.	Solvent-Naphtha I.	Solvent-Naphtha II.
	Marks.	Marks.	Marks.	Marks.	Marks.	Marks.
1906	18·60	24·60	39·80	27·66	21·18	18·79
1907	19·18	25·18	40·02	31·62	21·99	22·14
1908	18·26	24·26	31·40	31·63	20·86	20·72
1909	14·55	20·55	25·57	27·85	17·30	18·68
1910	14·55	20·55	25·57	27·85	17·30	18·68

APPENDIX I

Synopsis of the Products obtained from Coal-tar.

In conclusion we give a synopsis of the Products obtained from coal-tar, with enumeration of the final products and the pages where a description of the respective substances is to be found:—



APPENDIX II

Official Recommendations to prevent Accidents in Tar-distillation Works.

The following rules were issued in 1903 by the English Home Office, consequent upon a report by the Inspectors of Factories, eleven fatal and ten non-fatal accidents having occurred within three years, mostly ascribed to the inhalation of sulphuretted hydrogen. Those specified in paragraph (2) are specially important.

(1) All uncovered tar reservoirs, wells, and tanks, unless constructed so as to be at least 3 ft. in height above the ground or platform, should be securely fenced with either a brick wall or double rail, to the height of 3 ft.

(2) During the process of cleaning, every tar-still should be completely isolated from the adjoining tar-stills, either by disconnecting the pipe leading from the swan-neck to the condenser worm, or by disconnecting the waste gas-pipe fixed to the worm end or the receiver. Blank flanges should be inserted between the disconnections. In addition, the pitch-discharge-pipe at the bottom of the still should be disconnected.

(3) Every still should be ventilated and allowed to cool before persons are allowed to enter.

(4) Every tar-still should be inspected by the foreman or other responsible person before any workman is allowed to enter.

(5) No person or persons should be allowed to enter a tar-still, or tank, unless provided with a belt securely fastened round the body with a rope attached, the free end to be left with two men outside, whose sole duty should be to watch and draw out any man in the tank who should appear to be affected by gas.

(6) A bottle of compressed oxygen, with mouthpiece, should be kept at all times ready for use, and printed instructions as to the use of the bottle, and the methods to be employed for resuscitation by means of artificial respiration, should be kept constantly affixed. A draft of such instructions is appended.

(7) A supply of suitable chemical respirators properly charged and in good condition should be kept ready for use

In case of emergency arising from sulphuretted hydrogen or certain poisonous gases. (Granules of carbon saturated with a solution of caustic soda readily absorb sulphuretted hydrogen, and may be used for charging respirators.)

(8) The use of naked lights should be strictly prohibited in any portion of the works where gas of an inflammable nature is liable to be given off.

(9) Each still should be provided with a proper safety-valve, which should at all times be kept in efficient working condition.

END OF PART II.

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CHAPTER X

LIGHT OIL

It was formerly the style of work followed at all British tar-works (as described *supra*, p. 440), to collect as the first fraction in distilling the tar all the oils obtained during the time that some water is coming over as well. This fraction is called *first runnings*, and that fraction which follows it, up to about 210°, is styled *light oil* (or *crude naphtha*).

During recent years some of the large British tar-works have adopted special processes for dehydrating the tar before its distillation, such as have been described *supra*, pp. 384 *et seq.*, and as are employed at most Continental works. In that case no separate collection of "first runnings" is made, but the first fraction is everything distilling over from the tar stills up to 170° or 180°,[1] and is styled "light oil." The following statements all refer to "light oil" as just defined.

Light oil is a thin, very easily flowing liquid, of yellow up to dark-brown colour, sometimes exhibiting a green fluorescence owing to a little mechanically carried-over tar, of sp. gr. 0·910 to 0·950, intensely smelling of ammonium sulphide, carbolic acid, and naphthalene. It commences boiling at 80° to 90°; up to 120° (which is the limit for aniline-benzol) 30 to 40 per cent., up to 160° (the limit for the xylols) 56 to 80 per cent. pass over; the remainder (up to 90 per cent.) comes over between 170° and 220°. The statements refer to the light oil obtained in distilling gas-tar; the light oil from coke-oven tar, according to Spilker, frequently contains oils boiling at higher temperatures.

---

[1] That means the temperature indicated by thermometers fixed in the space *above* the tar. Thermometers the bulb of which is *immersed in the tar* will indicate up to 200°, at which temperature the water is split off from the phenol hydrates.

This difference comes out very clearly in the following distillation results from light oils of gas-tar and coke-oven tar, quoted by Rispler:—

Distilling	Light oil from	
	Gas-tar.	Coke-oven tar.
°C.	Per cent.	Per cent.
Up to 100 . .	10	6
,, 135 . .	47	29
,, 165 . .	69	42
,, 195 . .	85	58

Components of Light Oil.

Kraemer and Spilker (in Muspratt-Bunte's *Chemistry*, viii., p. 16) enumerate in "light oil" (in the sense defined *supra*):

1st. 5 to 15 per cent. *phenols*, viz., carbolic acid and cresols (principally metacresol), but hardly any xylenols.

2nd. 1 to 3 per cent. *bases*, viz., principally pyridine and its homologues, with a small quantity of aniline, traces of pyrrol, and perhaps of indol.

3rd. 0·1 per cent. *sulphur compounds:* carbon disulphide, thiophen and its homologues.

4th. 0·2 to 0·3 per cent. *nitriles* (acetonitrile and benzonitrile).

5th. 1·0 to 1·5 per cent. *neutral oxygenated compounds:* acetone, cumarone.

6th. *hydrocarbons*, forming the principal portion, and composed of:—

(*a*) 3 to 5 per cent. olefins.

(*b*) 0·5 to 1·0 per cent. paraffins, from hexane upwards.

(*c*) 1 to 1·5 per cent. non-saturated cyclic compounds, combining at ordinary temperatures with bromine (cyclopentadiene, dicyclopentadiene, dihydrobenzene, tetrahydrobenzene, styrol, indene—the latter sometimes in considerable quantities).

(*d*) Traces of saturated cyclic compounds (hydrindene, etc.).

(*e*) The remainder, *i.e.*, 80 per cent. of the light oil, consists of aromatic hydrocarbons, of which about four-fifths belong to the benzene series and one-fifth to naphthalene and other higher-boiling hydrocarbons. The proportion of the benzene hydrocarbons in what Kraemer and Spilker term "light oil"—that is, in our light oil plus first runnings—is stated by them to be about 100 benzene, 30 toluene, 15 dimethylbenzenes (xylenes), 10 trimethylbenzenes, 1 tetramethylbenzenes, traces of higher methylated and ethylated benzenes.

When being worked up, the light oil yields, in round figures, the following commercial products:—

60 to 65	per cent.	benzols.
12 „ 15	„	naphthalene.
8 „ 10	„	phenols.
1 „ 5	„	pyridine bases.

The remainder is accounted for by "neutral oils" and the unavoidable losses in distillation. Light oil, therefore, is the principal material for obtaining benzene and its homologues, and to a smaller extent for naphthalene, phenols, and pyridine bases.

Applications of Light Oil as such.

A good deal of light oil is used up without purification—*e.g.* for illumination in excavations (where the smoke is of no consequence), for thinning down heavy oil or liquefying pitch to make "refined tar," and especially for preparing varnishes for wood and iron (pp. 548 *et seq.*). Thenius (*Verwertung des Steinkohlentheers*, p. 62) makes from it "varnish oil" by treating it several times with potassium bichromate, manganese, and sulphuric acid, then with water, at last with caustic-soda liquor, and subsequently distilling. Thus a limpid oil of sp. gr. 0·880 is obtained, which does not turn yellow in the air and is an excellent solvent for resins like sandarac, mastic, or copal; so that superior varnishes for photographers and printers, cart-grease, lubricating oil, etc., can be prepared with it, for which special prescriptions are given.

Manufacture of Benzoic Acid from Light Oil.

Benzoic acid, which had been found in the residues from the carbolic acid manufacture by K. E. Schulze, and which is formed from the benzonitrile present in the tar-oils, can be manufactured from light oil according to the Aktien-G. f. Teer- u. Erdöl-Industrie (Ger. P. 109122) by the following process:—The fraction boiling between 150° and 240° C. is freed from phenols by washing with caustic-soda solution, sp. gr. 1·10. The oil is now heated by injection of steam with about twice as much caustic-soda solution, sp. gr. 1·4, as is required for saponifying the benzonitrile present, in a still provided with a steam jacket and inside open steam-pipe and a stirring apparatus, until all the ammonia is expelled. This takes a few hours. The distillate contains the more volatile oils and ammoniacal liquor. The liquid remaining in the still on cooling separates into an oily and an aqueous portion. The latter is treated with gaseous CO_2, until the excess of NaOH has been saturated, and the small quantity of phenols, appearing as an oily layer on the top, is removed. The clear aqueous liquid is an almost chemically pure solution of sodium benzoate, from which benzoic acid is obtained by adding a stronger acid in the shape of fine white crystals.

Treatment of Tar-oils with Phosphoric Acid.

According to the Fr. P. 443650, and additions; B. Ps. 9856, of 1912, and 5484, of 1913, of Melamid & Grötzinger, the impurities of mineral oils can be separated by treating the oils with phosphoric acid, or a mixture of this with pyrophosphoric and phosphorous acids, preferably at temperatures from 150° to 200°, subsequently raised to 300° to 400°. According to their Ger. Ps. 264811 and 276765, the hydrocarbons of tar-oils are converted into hydrocarbons of lower boiling point by heating with 25 per cent. phosphoric acid, and repeating this treatment. For example, one kind of tar yielded 6·5 per cent. oils, boiling up to 200°, sp. gr. 0·950; but when heated with 25 per cent. phosphoric acid, it yielded 30 per cent. oils, boiling below 200° (sp. gr. 0·897), 9 per cent. up to 230° (0·900), 23 per cent. up to 270° (0·992), and 14 per cent. up to 320° (sp. gr. 0·860), etc., etc.

Working-up of the Light Oil.

The light oil is, to begin with, treated just like the middle oil, as described in the last chapter. It is once or twice redistilled in a still, heated by means of an ordinary fire-grate, breaking up the distillate into several fractions, and treating these for the removal of acid and basic substances, mostly also in apparatus like that used for the middle oil. This is, however, followed by a chemical treatment of the neutral oils with concentrated sulphuric acid and alkalis, and ultimately a decomposition of the compounds formed by means of steam into their constituents, and preparation of these in a pure state by means of quite exactly working column-apparatus. We shall now describe the single stages of this process.

Stills for Light Oil.

The rectification of light oil is effected in wrought-iron stills, usually constructed and set exactly like tar-stills. The bottoms are, however, never made so much curved-in as shown in Fig. 81, p. 401, because much less is left in the still when distilling light oil than when distilling tar. Only at the largest works are they made as large as the tar-stills; at others a small size suffices, as only a small percentage of the tar passes through them. *E.g.*, a still 5 ft. wide and 6 ft. high suffices for four tar-stills of twice the height and width. It is preferable not to go below the size just mentioned, even at smaller works, but rather to work the still less frequently, or to employ it at the same time for the first rectification of the crude benzol. The reason for this is that such a still, holding about 750 gall., can be easily worked off in a working-day, say seven to nine hours, and allowed to stand overnight, to cool down the residue before running it out. The still-top is covered with brickwork or some non-conducting material. The still-head is made of cast-iron, and is connected with a 2-in. lead worm, ending in a 1½-in. lead worm, the lower part of which may be only 1 in. wide. A condensing-tub 4 ft. wide and 6 ft. high suffices for such a still. It should be separated by a wall from the still, likewise the two receivers for naphtha and secondary light oil; the discharge-cock also is best made to pass through the wall, so that all these parts are away from the fire and can be seen at a glance. Fig. 180 shows this arrangement.

The discharge-pipe for the residue can be provided with a screw-thread, in order to connect it directly by means of a pipe with the tank for carbolic or creosote oil. This is done, because the residue is very hot, even after standing overnight, and gives out very acrid and disagreeable vapours.

Of course the usual *mountings* must be provided, such as manhole, feed-pipe, air-vent, and thermometer; a simple safety-valve (p. 416) should also be put on.

Some manufacturers prefer heating the light-oil still by *indirect steam;* but this does not seem to offer any advantage. It is useful, however, already at this stage to substitute for an ordinary still-head a *dephlegmating column*, so as to effect a better separation of the product, as we shall see in the next chapter. This is especially advisable when first runnings and light oil are rectified together.

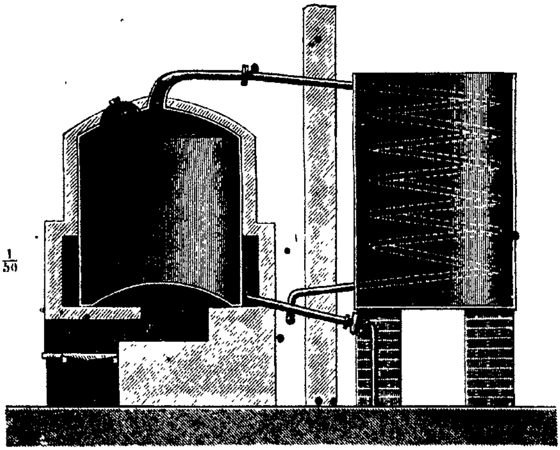

Fig. 180.

Working the Light-oil Stills.—When working a light-oil still, a brisk fire is made at first; but this is moderated as soon as the distillation begins, and is raised again later on. Here, too, some water comes at first; but ceases again after a short time. As long as naphtha comes over, say up to 170° or 175°, cold water must be run through the condensing-tub; but after this the water in the latter and the distillate should be allowed to get warm, because very much naphthalene comes along, and might choke up the worm if it solidified. We have seen (p. 833) that it is still [illegible]cessary to prevent this when distilling the oil taken away from sodium phenolate. Special care should be taken to shape the end of the worm so that the distillate can run out completely; otherwise, at the end of the operation a plug of naphthalene will be formed there, which might be overlooked in starting a new operation, and might lead to awkward consequences, especially in the absence of a safety-valve. It even happens, if the still is cooled down too much before discharging, that the residue solidifies entirely and cannot be run out without heating the still again.

Fractionation.—The object of the first rectification of the light oil is not the preparation of commercial products; for this the composition of light oil is still too complicated. For similar reasons it was formerly believed that it did not pay to wash it chemically, except when it had been purposely collected up to the point at which it contains much carbolic acid; and frequently even then its last portions only were treated with alkali. Hence the usual object of rectifying it is, on the one hand, to obtain the most volatile oils (which belong to the same class as the "first runnings" and are treated together with these), and, on the other hand, to separate the heaviest oils which promise no further yield of benzol and go better to creosote or carbolic oil. Between these two a fraction necessarily remains which exhibits some of the characteristics of both. This is always put back into the still and distilled with light oil; so that the latter is finally completely split up into the two products mentioned above, although in each single operation three products are obtained, which we call *light-oil naphtha*, *secondary light oil*, and *residue*. This has caused almost all tar-distillers to make two fractions in the distillation of light oil, and to run the third product, as residue, directly out of the still. The question can only be, where to set the limits. Evidently, if the residue is to go to creosote oil, the distillation must be continued till no appreciable quantity of light oil remains behind; and this indicates the limit between the second and third fractions. Where the residue goes to carbolic acid, not even the above is of consequence, since the alkaline treatment in any case separates the hydrocarbons contained in it. In the former case the usual test is, to work till the distillate begins to sink in water; in the latter case the thermometer is usually consulted (see below).

It is more uncertain where to set the limit between the first and second fractions. Evidently this does not matter very much, since the second fraction is always redistilled. Some English tar-distillers go by the hydrometer, and change the receiver when the distillate shows 10 degrees "under-proof" (*i.e.*, sp. gr. 0·932), at which point about one-fourth part of the light oil has distilled. The second fraction is collected till it begins to sink in water, which corresponds to another 25 per cent., sometimes to 50 per cent. of the light oil.

The *first fraction* (*light-oil naphtha* or *twice-run naphtha*) from light oil obtained in the first distillation of tar shows, for example:—

	Boiling-point.	Per cent. distilling at								
		28°.	100°.	110.	120°.	130°.	188°.	149°.	160°.	171°.
1	92°	...	...	2½	9	20	33	50	64	78
1*a*	84°	2½	5	12	24½	33	39	...	...	...
2	107°	...	...	1	5	17	29	47	64	79
3	104°	...	...	½	3	10	21	44	63½	78
3*a*	98°	...	4	...	...	..	...	...	...	...
4	101°	...	...	4	19	38	52	68	79	90
5	107°	...	...	1	5	17	29	47	64	79

1*a* is the result of rectifying the first 50 per cent. of 1; 3*a* that of rectifying the first 50 per cent. of 3. According to this there are great divergencies in the intermediate products; but finally in all cases, nearly 89 per cent. has come over at 171°. The distillations 1*a* and 3*a* show that from light oil toluene, xylene, etc., can be obtained, but no considerable quantity of benzene.

The oils taken off from sodium phenolate naturally show rather higher boiling-points, as proved by the following example, where 1 indicates the distillation of the oil itself, 2 the rectification of the first 41 per cent.:—

	Boiling-point.	Per cent. distilling at								
		93°.	100°.	110°.	120°.	180°.	188°.	149°.	160°.	171°.
1	118°	...	...	...	...	6½	21	41	58	72
2	...	...	...	5	15	25	32½	...	...	...

Davis (*J. Soc. Chem. Ind.*, 1885, p. 646) quotes the following tests of "twice-run naphtha":—

	Spec. grav.	Per cent. distilling at					
		100°.	110°.	120°.	140°.	170°.	200°.
a	0·878	0	17	41	72	94	99
b	0·888	3	23	46	71	88	95
c	0·901	2	20	40	62	80	90
d	0·904	0	9	29	57	81	95

At the (English) tar-works managed by myself the fractionation differed according to the final products required. If so-called "90 per cent. benzol" (*vide infra*) was to be made, the first fraction was made at 110°, the second at 140°, and the third at 170°. The first fraction in this case gives much 90 per cent. benzol in the distillation by steam. If, however, the product required was "50 per cent. benzol," only two fractions were taken, No. I at 140° and No. II at 170°. It is advisable not to go beyond 170°, but to leave the residue in the still to cool down over night, and work it up together with the "middle oil."

The French style of work is described by Wurtz (*Dictionnaire de Chimie*, i., p. 1633). According to him, the fraction of tar distilling between 150° and 200° (roughly corresponding to our light oil) is worked up thus:—

First Rectification.

a. Fraction up to 120° goes to the corresponding fraction of the principal distillate, received up to 150°.

b. Fraction between 120° and 190° is washed with acid and alkali, then rectified.

c. Residue (above 190°) goes to creosote oil.

Second Rectification (of the fraction *b*).

a. Product up to 120° contains benzene and toluene, goes to the corresponding products from the first runnings.

b. Product from 120° to 127° yields solvent naphtha No. I.
c. „ „ 127° to 140° „ „ „ „ II.
d. „ „ 140° to 150° „ „ „ „ III.
e. Residue goes to creosote oil.

The product distilling from light oil at 170° to 210° and above, called "secondary light oil," is sometimes employed for washing anthracene (p. 612); or it is chemically washed and rectified, so as to yield "solvent naphtha" and oil for absorbing benzol from coke-oven gases.

As to the processes followed in Germany, we quote the following statements from Spilker and Rispler. According to Spilker (*loc. cit.*, p. 54) the light oil is rectified in wrought-iron stills, directly heated, of the same shape as the tar-stills (but of smaller size), and set in the same way. In lieu of the man-hole there is a "hand-hole," 8 in. wide, and in lieu of the arched top there is a rectifying-column, 6 to 10 ft. high and 1·6 to 3·3 ft. wide. According to Rispler (*loc. cit.*, p. 545), the contents of the light-oil stills vary from 10 to 17 tons; the column is 13 ft. high and usually 3·3 ft. wide. One light-oil still, 6 ft. high and 5 ft. diameter, suffices for treating the light oil produced by four tar-stills twice as high and twice as wide. It is not advisable to use light-oil stills of smaller dimensions than those just indicated; even at smaller factories it is preferable to make the light-oil still of that size, and to work it at intervals, or use it also for rectifying the crude benzol (*vide infra*). Such a still, which holds about 3500 litres, can be worked off in seven to nine hours, and allowed to stand overnight to give the residual oil time for cooling before drawing it off.

According to Spilker, the distillation is best carried on in such a way that about 250 litres pass over per hour; hence a still holding from 2000 to 3000 litres will require twelve hours, and a still holding from 4000 to 6000 litres twenty-four hours for being worked off. The long time required for working the light-oil stills, and the very much higher cost of it for fuel, etc., in comparison with the distillation of the tar itself, are caused by the slow rate of distillation and the dephlegmating action of the column.

The same author gives the following rules for the fractionation of the light oil:—The first break is made when the thermometer in the still shows 135°, or, if working by the hydrometer (which is the usual case), when the distillate shows the sp. gr. 0·89. This is the *crude benzol No. I* or *light benzol.* The second fraction goes up to

165°, or sp. gr. 0·95; this is the *crude benzol No. II* or *heavy benzol.* The third fraction goes up to 195° or 200°, sp. gr. 1·00; this is "carbolic oil." The distillation is stopped as soon as there is a strong separation of naphthalene in the distillate, and until a sample, cooled down to 15° in a test-tube, solidifies to such an extent that on turning the tube upside down nothing runs out of it. The residue thus remaining in the still is run off while still warm, and worked up together with the middle oil; the "carbolic oil," taken as the third fraction, is worked up together with the corresponding fraction of the middle oil, and fractions I and II go into the benzol department of the factory.

The following tests of these fractions are quoted by Kraemer and Spilker:—

Light benzol has an average sp. gr. of 0·880 and, on boiling, yields about 90 per cent. from 80° to 140°, *e.g.*:

Up to 80° . .	0 per cent.	Up to 115° . .	76 per cent.
„ 85° . .	3 „	„ 120° . .	80 „
„ 90° . .	21 „	„ 125° . .	83 „
„ 95° . .	39 „	„ 130° . .	86 „
„ 100° . .	57 „	„ 135° . .	88 „
„ 105° . .	63 „	„ 140° . .	90 „
„ 110° . .	70 „		

It contains about 2 per cent. acid oils (phenols), and rarely above 1 per cent. bases (pyridine, etc.); moreover, all the carbon disulphide of the crude tar, and variable quantities of low-boiling aliphatic hydrocarbons. *Heavy benzol* has an average sp. gr. of 0·93 and, on boiling, yields:

From 125 up to 130°.	10 per cent.	Up to 160° . .	70 per cent.
„ 140°.	20 „	„ 170° . .	80 „
„ 150°.	45 „	„ 180° . .	90 „

It contains between 2 to 4 per cent. bases, and between 5 to 10 per cent. phenols.

For recovering the acid (phenols) and basic components, these two fractions are submitted to the same successive treatment with caustic soda and dilute sulphuric acid, and in the same apparatus, as has been described in Chapter IX. for the treatment of carbolic oil. But whilst the "light benzol" after this treatment is mostly at once subjected to the "chemical purification," as described *infra*, the "heavy benzol," in order to economize chemical agents and to simplify the further working-up, is usually once more distilled in the light-oil still, as described *supra*, which furnishes fractions of the same kind as those obtained from light oil, and are worked up with these. Moreover, a fraction is obtained, boiling between 160° and 190°, which is known as "commercial heavy benzol," and which, after being washed with 1 to 3 per cent. sulphuric acid, goes into the trade as *solvent naphtha*.

The just-given description does not apply to the distillates, containing benzol and its homologues, obtained from the saturated *benzol-washing oil of coke-oven gases*. When continuously distilling this oil in column-apparatus, products of much more uniform quality are obtained. Thus, *e.g.*, Wilhelm (*Z. für chem. Apparatenkunde*, 1907, p 33) describes a rectifying-column for such products, worked by open steam, furnishing immediately, without chemical washing, a crude benzol boiling at the same points as commercial 50 per cent. benzol. This product, after being separated from the ammoniacal water condensed from the steam, goes at once to the column-apparatus for commercial 90 per cent. benzol, from which continuously such benzol distils off, whilst the products boiling at higher temperatures run off into a lower still, where they are converted, also continuously, into corresponding commercial products. The vapours escaping from the stills are thus, by means of suitable column-apparatus, and after being separated from water, converted into commercial crude 90 per cent. benzol, toluol, solvent naphtha, etc.; the residues collecting in the stills are run into cooling-tanks, where they separate into solid naphthalene and liquid oils, which go to the washing-oil. The chemical purification of the hydrocarbons in this case, therefore, is only effected after the fractionation in steam-heated columns, from which they are obtained nearly pure, or at least in such a shape that no further distillation is required for fulfilling the demands as to boiling-points made in the trade.

According to Schreiber (*loc. cit.*, p. 47), the benzol obtained from the coke-oven gases in Lower Silesia is first washed with sulphuric acid, and then neutralized with caustic-soda solution, sp. gr. 1·03, or milk-of-lime made from 160 to 180 kg. CaO per 1 cbm. water; the latter is much cheaper, and equally efficient. The washing takes place in lead-coated cast-iron vessels, with a slightly inclined conical bottom, and a ship-screw agitator fixed to the top, holding 10 tons. The agitator makes 60 turns per minute; the washing takes place in three or four stages of an hour each. The consumption of acid is 7 per cent. for benzol and toluol, and 10 to 12 per cent. for solvent-naphtha. The loss by washing is 7 to 8 per cent. in the case of benzol and toluol, 20 to 25 per cent. in that of solvent-naphtha.

FIRST RUNNINGS (LIGHT NAPHTHA).

This term is applied to the first and lightest distillate from the tar-still which comes over together with some (ammoniacal) water, as described on p. 445; and we shall now show how it is further treated. This fraction is sometimes called first light oils, or once-run naphtha, or crude naphtha, etc. Where no such fraction is made, but the light oil is collected all together, it is generally redistilled over a direct fire; and the "twice-run naphtha" or "light-oil naphtha" thus obtained is treated in a similar way to that now described for our "first runnings."

The latter product contains, of course, the most volatile constituents of coal-tar, as enumerated in the third chapter; but along with them, owing to the peculiar nature of fractional distillation, there are considerable quantities of less volatile bodies. Hence we find in it not merely benzene and its homologues, but sensible quantities of thiophens, of phenols, naphthalene, aniline and other bases, empyreumatic resins, etc. Some of the most volatile bodies are impurities to be removed as completely as possible, as methane homologues, thiophens, olefins, carbon disulphide, mercaptans, nitriles. The "eupion" sometimes mentioned, and Mansfield's alliol, will have to be sought among the latter class of bodies.

Since a distinction or separation of all these bodies is not to be thought of, least of all for technical purposes, it is usual to estimate the quality of first runnings by fractional distillation exactly in the same way as described above (pp. 860 *et seq.*) for light oil, rectifying again the more volatile portion. The following table shows some of the results thus obtained, in percentages by volume:—

No.	Boiling-point.	88°.	98°.	100°.	110°.	120°.	130°.	138°.	149°.	160°.	171°.	Sp. gr.
1	79°	1	2½	4½	12½	22½	31	37	45	52	62	0·906
2	84°	1	...	15	30	43	51	57	63	69	77	...
3	93°	...	...	2	...	27	43	54	63	73	83	0·905
3*a*	...	...	3	15	...	...	...	...	...	...	...	...
4	91°	...	3	10	26	38	49	55	63	71	78	0·908
5	89°	...	½	5	34	45	55	61	68	73	78½	0·911
5*a*	...	...	9	27½	40	47½	...	...	...	...	...	...

In all these tests the thermometer-bulb at the beginning of the distillation was just immersed in the liquid; the "boiling-point" is consequently much higher than the temperature at which the vapours actually passed over; and even the later temperatures are no doubt too high. 3*a* is the result of rectifying the first 45 per cent. of 3; 5*a*, that of the first 61 per cent. of 5.

The table shows that the composition of first runnings varies very much, especially at the lower temperatures, without being indicated by the specific gravity. In fact, the latter is quite worthless for the estimation of the commercial value of crude naphtha. A single distillation of the latter does not suffice; and in any case that which has passed over up to 130° should be rectified. Even then the results differ considerably if, as is usual in England, the thermometer-bulb is immersed in the liquid, according to the size of the retort, the quantity of the liquid, etc. The only reliable plan is to place the mercury-bulb at the height of the vapour-delivery tube; and it is even preferable to work with a proper fractionating-flask connected with a Liebig's cooler (Fig. 181); best of all with a dephlegmating head, such as Linnemann's three-bulb apparatus (*cf.* next chapter). It has been found the most suitable plan to place the mercury vessel exactly as figured here—that is, its top on a level with the bottom of the side-tube.

More accurate methods for testing the value of crude naphtha will be described at the end of Chapter XI.

Good first runnings in the first distillation ought to yield at least 10 per cent. by volume up to 100°; in rectifying the product distilled up to 130°, at least 25 per cent. should come over up to 100°. Up to 171°, on an average 78 per cent. comes over.

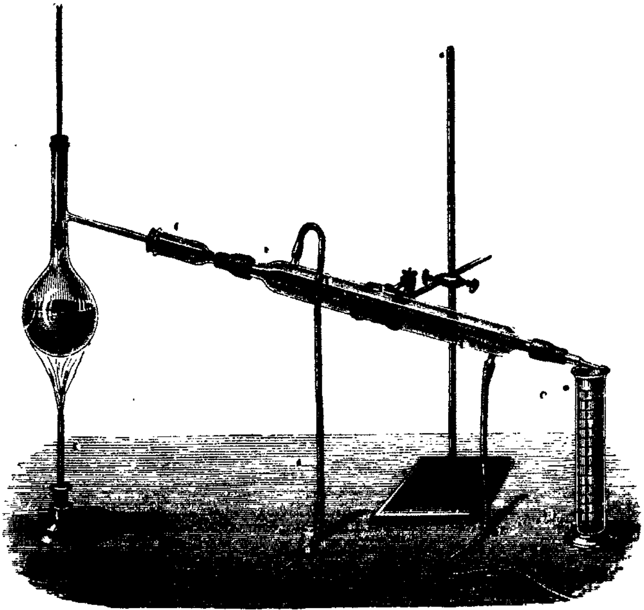

FIG. 181.

Watson Smith found the following results of first runnings from Wigan cannel-coal tar:—

Below	130°	130-140°	140-150°	150-160°	160-170°	170-180°	180-190°
Per cent.	15	20	10	6	9	7	11

Hokenhausen (*J. Soc. Chem. Ind.*, 1884; p. 73) quotes the following tests:—

A. *English Naphtha.*

Centigrade.	Wigan. Per cent.	Yorkshire. Per cent.	Scotland. Per cent.
105°	...	4	...
110°	4	16	17
120°	19	34	38
130°	33	47	49
140°	45	...	58
150°	55	...	69

B. *French Naphtha.*

Centigrade.	D'Anzin. Per cent.	Blanzy. Per cent.	Comp. Par de Gaz. Per cent.
100°	5	14	10
120°	24	37	23
130°	39	49	55
140°	50	59	75
150°	60	69	90
160°	67	77	98
170°	75	85	...

Davis (see below) quotes as the average of many tests of first runnings from different parts of England:—

Sp. gr.	100°	110°	120°	140°	170°	200°
0·905	2	14	33	57	80	92

Washing with Chemicals.

The first runnings, as well as the light-oil naphtha, which is chemically quite analogous to it (*cf.* pp. 861 *et seq.*), is nearly always "chemically washed" before any rectification, *i.e.*, treated with strong sulphuric acid and alkali, less frequently with oxidizing agents. Formerly the greatest stress was laid on washing the naphtha with *strong sulphuric acid*, and this treatment was applied to the naphtha first and foremost. It was always followed, first by washing with water and then with a solution of alkali, before proceeding to the final treatment in the steam-stills. In that style of proceeding the phenols could not be recovered, since they are (together with the naphthalene) converted into sulphonic acids which remain dissolved in the acid (acid-tar). The pyridine bases were, of course, also taken up by the sulphuric acid, but it is difficult to recover them from the acid-tar, and this was never even attempted on the large scale at that time, as there was no use for those bases. The sulphuric acid also takes up the olefins and part of the thiophen and its homologues, a little acetone, other ketones, nitriles, etc.; it destroys empyreumatic resinous substances, and so forth. It acts also upon the valuable substances, viz. benzene and its homologues, but at the ordinary temperature only to an insignificant extent; if no more acid is employed than is necessary, still, as this action is never entirely absent, it should not be prolonged beyond necessity, and no excess over and above the quantity required for purification should be employed. Used in excess, sulphuric acid forms "sulpho-oils," *i.e.*, partly sulphonic acids, partly sulphones, *e.g.*, $(C_6H_5)_2$ SO_2, which to some extent remain dissolved in the hydrocarbons and are afterwards very troublesome, especially in burning. I have experimentally proved (*Chem. Zeit.*, 1883, pp. 5 and 57) that, under the same circumstances, the action of sulphuric acid in dissolving the benzenoid hydrocarbons is stronger in the case of the higher homologues than with benzene itself. When treated for five minutes with 5 per cent. of strong sulphuric acid, benzene loses 0·1 per cent. (when quite free from thiophen, even less), but xylene 0·25 per cent. The quantity of hydrocarbons dissolved increases with the quantity of acid employed and with the temperature. After being treated with sulphuric acid, benzene assumes a yellowish, toluene a greenish, xylene a pink colour; but all these colours vanish after washing with water. Kraemer and Spilker have shown that one of the principal actions of sulphuric acid is the condensation of cumaron, indene, and cyclopentadiene into resinous polymers, and a molecular combination of styrolene with the methylated benzenes. (This reaction is utilized by the Aktien-Gesellschaft für Teer- und Erdölindustrie, Ger. P. 53792, as mentioned *supra*, p. 282.) The reaction is not yet cleared up in all particulars, but evidently differs with the difference of the substances. Cyclopentadiene (boiling-point 40°) and dicyclopentadiene (boiling-point 170°) are transformed into a dark brown resin, insoluble in all solvents, which soon separates from the sulphuric acid and transforms this into a magma, so that great haste is necessary to draw off the acid. The olefines at first simply add H_2SO_4, forming ether-sulphuric acid, which partly remains dissolved in the sulphuric acid, partly reacts with another molecule of the olefine, forming a neutral sulphuric-acid ether or else splitting off sulphuric acid and forming a polymeric olefine. Other substances may be again formed from these, but probably the polymeric olefines are formed in the greatest quantity. They remain dissolved in the benzol and are found in the residue when fractionating it. The free ether-sulphuric acid is decomposed, when afterwards water is applied for washing with formation of an alcohol:

$$C_6H_{12}\begin{matrix}-OH\\-SO_3H\end{matrix} + H_2O = C_6H_{13}(OH) + H_2SO_4.$$

The application of *alkali* (practically always caustic soda) is quite as indispensable in the case of first runnings as in the purification of petroleum, paraffin oil, or the heavier coal-tar oils, although the first runnings contain a much smaller quantity of phenols, the removal of which is the principal object of this treatment. This made it possible, and formerly most usual, to commence the washing with sulphuric acid and end with weak caustic-soda liquor. The latter can in no case be dispensed with entirely, as it must remove the remaining phenol and every remnant of sulphuric acid and sulphonic acids.

Recently it has become most usual to *commence with the alkaline treatment.* This allows of recovering the phenols, and is evidently quite indispensable when first runnings and light oil have not been separated in distilling, but are washed together before rectifying. It must, moreover, be borne in mind that the phenol contained in first runnings is mostly real carbolic acid, and is all the more valuable because of this. On the other hand, it has been asserted that phenol made from first runnings alone has a very disagreeable smell, and very probably this is really the case; but this objection is avoided if the alkali previously used for washing first runnings is mixed with fresh caustic-soda solution, and is subsequently employed for washing light oil or carbolic oil, as described on pp. 731 *et seq.* On the whole, it seems advisable to proceed in this way; that is, to begin with alkali of, say, sp. gr. 1·15; then comes sulphuric acid of about 1·3 sp. gr., to extract the pyridines; this is followed by a treatment with strong sulphuric acid, sp. gr. 1·84, to remove the non-saturated hydrocarbons, etc.; and the last washing takes place with a weak solution of caustic soda.

The mixing-apparatus for the chemical treatment of crude naphtha must, of course, be proof against the action of acids and alkalies. Formerly it was usually made of wood or sheet-iron lined with lead, the sheets of lead being burned together by the hydrogen-blowpipe. The lead coating is ¼ to ⅜ in. thick. But recently cast-iron vessels are preferred, which do not so frequently need repair as leaden ones. Cast-iron is but slightly acted upon by the strong vitriol, and even less so when the latter is charged with tarry matters. Hence cast-iron machinery can be employed for agitation (mixing); and the discharge-cocks may even be made of brass or gun-metal, which would be impossible in the case of pure acid.

The mixers must be well covered over, to prevent the benzol from volatilizing during the operation. In the case of hand work this cannot be carried out so completely as with mechanical stirring, where the shaft passes through a stuffing-box and special pipes are provided for running-in the naphtha, acid, water, and alkali.

The discharge-cocks should always be so arranged that the dirty acid, as well as the water, can be run out to the last drop. For this purpose the bottom is made to slope to one side, and the cock is fixed in the lowest part in such a way that no portion of it projects upwards; so that any mixture of the liquids in running out can be entirely avoided with some little care.

At small works the mixing of the naphtha with the chemicals or the water can be done sufficiently *by hand*, especially as only a small percentage of the tar is subjected to it. This is performed by means of wooden rakes, the head of which is about 15 × 6 in., and is perforated with six or eight 1-in. holes; with these the attendant constantly fetches the acid, etc., up from the bottom, which mixes it much better than mere stirring. This should be continued for an hour, or for half an hour at least. In this case the mixer may be circular or square, whilst for mechanical mixing it should be circular. It should be only three-quarters filled with the naphtha to be washed.

Evidently mixing by hand is very inferior to *mechanical mixing*, which is, indeed, preferred at all larger works. Sometimes it is done by a finely divided current of air (as described *supra*, p. 738, for carbolic oil); but most manufacturers prefer agitating by machinery, because the current of air carries away some benzene. This cannot amount to very much, as the mixing need not last above ten or fifteen minutes. We shall mention only some of the most frequently used mixing-machines. We have already (p. 738) spoken of Hübner's machine, constructed like a churn, in which the mixing is effected by a perforated piston, moving up and down, similar in principle to the mixing by hand with perforated rakes just described. A similar principle was employed in Jung and Must's apparatus,[1] with the exception that the motion was not communicated by gearing, but by a steam-cylinder placed directly on the mixer, the piston being attached to the same rod as the mixing-disk. Rolle's mixing-machine[2] consists of a sloping cast-iron cylinder, whose centre of gravity is situated in the agitating-shaft, provided with scoops for catching the acid and alkali, which, owing to their higher specific gravity, move at the periphery. This machine, as well as that constructed by Vogt,[3] seems less adapted for our purpose than either Hübner's or Jacobi's.[4] In the latter (Fig. 182) the cast-iron cylinder *a a* is surrounded by a wrought-iron steam-jacket, *b b* (which can be dispensed with for naphtha, but is indispensable for carbolic acid, naphthalene, etc.), and has a conically shaped bottom. In this tapering part revolve the

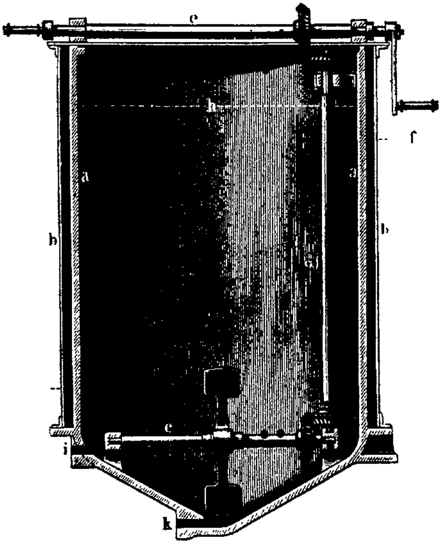

FIG. 182.

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[1] Described by Fuhst, *Dingl. polyt. J.*, clxvi., p. 21.

[2] *Wagner's Jahresber.*, 1862, p. 680.

[3] *Dingl. polyt. J.*, clxvii., p. 261 ; Jacobi (*ibid.*, clxviii., p. 264) declares it to be quite useless.

[4] *Dingl. polyt. J.*, clxviii., p. 261.

blades of a horizontal shaft, *c*, which is moved by a lateral vertical shaft, *d*, so that the contents of the mixer are quite accessible. In the arrangement shown in the diagram no stuffing-boxes are employed, because the packing could not be made to stand the action of acids, and the latter soon corroded the journals so that no tight joint could be effected. Lining with lead or asbestos packing did not prevent this in the case described by Jacobi, but I have seen several cases where it has been successful. The steam for heating enters at *f*, and the condensation-water issues at *g*; *h* shows the level of the liquid; *i* and *k* serve for discharging the oil and the washing-agents. The vessel *a a* should be cast in one piece, and with the bottom turned downwards, in order to avoid flaws, which would be very injurious in presence of the acid. The shaft *e* revolves forty-five or fifty times, the agitating shaft *c* sixty-four or seventy-two times per minute. This apparatus, which holds 3 tons, can be set in motion by two men, without any steam-power, as the mixing only lasts a few minutes at a time.

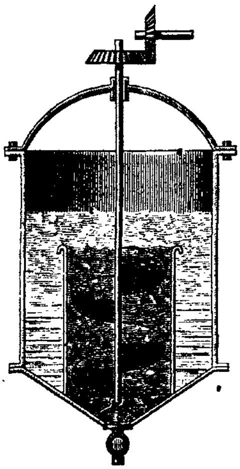

FIG. 183.

A very efficient form of mixer is shown in Fig. 183. The mixing vessel contains a smaller cylinder, open at top and bottom, and in the centre there is a spindle, carrying an Archimedian screw. By the revolution of the latter the acid or alkaline liquor, which is always at the bottom, is raised up in the inner cylinder and poured out over the top into the naphtha contained in the outer vessel. As it sinks down, it is caught up again by the screw, and thus a very good mixture is effected.

A similar mixer of special construction has been patented by Burt, Boulton, & Haywood, and E. R. Garrett, and is shown in Figs. 184 and 185, where the liquid can be made to move either in an upward or a downward direction.

Other mechanical mixers have been constructed by the following inventors:—

Kendall and others, U.S. Ps. 1154516 and 1154517.

Kraemer and Spilker (Muspratt's *Chemie*, 4th ed., viii., p. 23) show a mixer, the bottom of which is formed as a cone, in order to facilitate the settling and drawing off of the acid resins. At the point of the cone there are two taps, a large and a small one. The former serves for quickly drawing off the purified oil and the bulk of the acid; the small tap (with a swan-neck outlet) for cautiously taking away the last portions of the acid.

The "Turbinenmischer" of the Draiswerke, at Mannheim-Waldhof, has in its semi-globular bottom part a turbine-wheel which takes up the materials in the centre and hurls them violently against the sides.

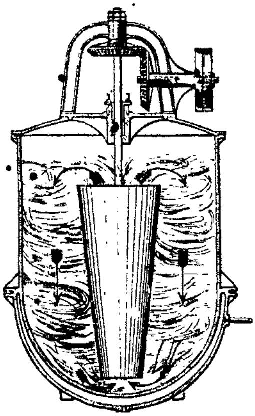

FIG. 184.

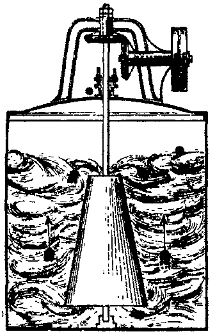

FIG. 185.

Sexauer (Ger. P. 185488) employs a vessel, in the centre of which a shaft, on which one or two perpendicular swan-neck pipes (open at top and bottom) are mounted, is revolving at a moderate speed. By the action of centrifugal force the lower, heavier liquid rises up through the pipes and comes out at the top in a continuous stream.

The mixer should be placed at a sufficient elevation to run both the acid and the other liquids into suitable places. The dirty acid is sometimes emptied into carboys, but is usually carried away to an outside tank by a lead spout.

The *washing-water* is not run straight away, as it is next to impossible always to prevent a little oil from coming along with it. This oil can be saved by the drain commencing in the mixing-house itself with a catch-pool, in which the washings are first collected. The floor is made to slope from all sides towards this catch-pool, so that any oil spilt anywhere can be washed into it. The liquid does not run into the drain from the top of the catch-pool, but through a pipe reaching nearly to its bottom, bent at an angle at the top and passing through its side into the drain. Since the drainage thus takes place from the bottom of the catch-pool, the oil remains quietly at the top, and is taken off from time to time.

Koppers (Amer. P. 1157988) describes an apparatus for treating benzene with sulphuric acid.

The *operation of mixing is performed in this manner*:—When the naphtha has been pumped into the mixer, it is first allowed to rest quietly for some time; and the never-failing water, which collects below, is completely drawn off before adding the washing chemicals, which would otherwise be diluted. A careful workman can, in this and all similar cases, run off the water without a drop of oil, by cautiously regulating the tap, observing the colour and touching the liquid with his finger. If any oil should run off through some mishap, it is retained in the catch-pool.

When it was usual to commence the chemical washing with strong oil of vitriol, the previous removal of the last traces of water from the naphtha was very important indeed. When, however, the beginning is made with an alkaline treatment (*supra*, p. 871), it is not quite so important to remove the last traces of water before this, but all the more so before proceeding to the treatment with concentrated sulphuric acid.

The *quantities* of alkali and acid used for chemical washing should be fixed by preliminary tests performed in the laboratory, as described on p. 732. Of course there must be always more taken than is just necessary for effecting the chemical reactions, as these are partly of a complicated and varying character, more especially in the case of concentrated sulphuric acid (*supra*, p. 869).

After completing the alkaline treatment, we come to the treatment with *sulphuric acid*. When, as now usual, the *pyridine bases are to be recovered*, the first acid employed is only of sp. gr. 1·3, as we shall see in the last part of this chapter. After this follows a treatment with 1 per cent. acid of sp. gr. 1·7, which is meant to take up the water, and this is again followed by the proper treatment with acid of sp. gr. 1·84, of which enough must be used to effect a thorough purification. We may commence with 2 per cent. of this strong acid, agitate for ten minutes, allow to settle, draw off the acid-tar (which occupies about twice the volume of the acid employed), add another 2 per cent. strong acid, and proceed as before. After this we should test the naphtha in the laboratory (which can be done during the hours required for settling) in the manner to be described hereafter, and if this test shows the necessity of applying another 1 or 2 per cent. of strong acid, this must, of course, be done before running the purified naphtha into another washer, where it is treated, first with water and then with dilute caustic liquor, as described below.

With a mixing-machine, ten or fifteen minutes suffice for thoroughly churning up the chemicals with the oil. After this at least three hours must elapse to allow the liquid to settle. It is best to mix at the end of the shift, and to let the liquid settle overnight, but not any longer, because otherwise the dirty acid turns so thick that it will not easily run out; sometimes great lumps of a pitch-like substance are formed, which choke up the tap. If the acid is too thick even after shorter settling, this is a proof that very many impurities were present—*e.g.*, tar which frothed over into the first runnings, or light oil from the light-oil still. In such a case more acid should have been used, and more alkali will have to be used afterwards. Thus even previous mistakes of the men can be subsequently discovered. On the other hand, if the dirty acid is too thin, this is a sign that too much acid has been used, or that the water had not been completely run off previously. Neither of these mistakes ought to occur. Generally the acid will be found to have doubled its bulk by taking up tarry matters.

Kirsch (Ger. P. 181255) describes a process for facilitating the separation of the resinous masses separated from the tar-oils by the action of strong sulphuric acid. His apparatus allows of heating the lower portion of the resinous mass and thus making it more fluid, while the upper portion is kept cool and more viscid, so that the mass is prevented from rising upwards into the oil. The greater fluidity also facilitates the drawing off of the acid-tar.

The acid should be run out to the last drop: the bottom of the mixer must be constructed accordingly (p. 874); for any remaining acid, on being diluted with the washing-water, separates a large portion of the dissolved bodies and thus contaminates the naphtha over again, certainly more mechanically than by solution, as the tarry matters, when changed by sulphuric acid, are hardly soluble in naphtha. For this reason alone the *dirty acid* or *waste acid* (also called *acid-tar*) must never be run off through the catch-pool and common drain (p. 875), which would be stopped up directly; it must be run by an open shoot into a special tank, or into carboys, tanks, etc. Wooden casks last some time, as the corrosive action of the acid is greatly weakened by its tarry admixtures; but they are acted upon in course of time. The acid should never be run straight into a public watercourse, as it is fatal to all animal life.

V. Falck (*Chem. Zeit.*, 1885, p. 1869) proceeds as follows in order to prevent naphtha from being carried away by the last portions of the acid in the form of an emulsion, and at the same time to avoid the contamination caused by adding water to the naphtha when still containing acid. After having drawn off the first acid-tar, he agitates the naphtha for fifteen minutes with 0·5 per cent. sulphuric acid at 142° Tw., draws off this acid, and repeats the operation with acid of 106° Tw. By diluting the waste acid in this manner, it is possible to remove the last traces with water or alkalis, without forming an emulsion.

The first treatment with strong sulphuric acid is followed by a second treatment with such acid. After three-quarters to one hour's agitation the liquid is allowed to settle, and the acid at the bottom is run off. This second washing-acid is forced up again by air-pressure, and used in the next operation for the first washing, so that all the acid which enters into the process is used twice over for washing the benzol. Even then it is not thrown away, but utilized for the manufacture of sulphate of ammonia, as we shall see later on.

When the acid has been drawn off, *washing with water* follows. Water amounting to about one-fifth of the bulk of the naphtha is run in, mixed up with it for a quarter of an hour, and allowed to settle for half an hour. The water, which has now acquired a deep red colour, is run off by the bottom tap, every precaution being taken against oil coming along with it, and flows away through the catch-pool sunk in the floor of the house (p. 876). This operation is repeated three or four times, and, if the fourth water is still coloured, even a fifth time. Even the fifth water tastes rather bitter, perhaps from naphtha; it may also react very faintly upon litmus; but it ought in no case to show any colour.

These washing-waters are utilized for diluting the strong acid-tar, which thereby separates into two layers. The bottom layer consists of a tolerably pure, although brownish acid of sp. gr. 1·30 to 1·35, which is used for extracting the pyridine bases, or in the ammonium-sulphate department of the factory. The upper portion is a thick solution of resin in benzol, containing some substances in suspense. It must anyhow not be run away, on account of its noxious properties, but neutralized with lime, whereupon the benzol may be recovered by a treatment with steam. The residue remaining behind is a resin, almost solid at ordinary temperatures, which may be used as a kind of asphalt for pavements, etc.

The total quantity of strong sulphuric acid required for purifying 90 per cent. crude benzol may amount up to 10 per cent. by weight, according to the quality of the benzol. The *loss of weight* of the benzol is about 7 to 12 per cent. in the case of 90 per cent. benzol, but it may be considerably greater in the case of the higher-boiling products. The loss of the mixture of first runnings and light oil, as it is now usually treated, through washing with sulphuric acid is on the average 8 per cent. by volume. In the case of good oils it may go down to 5, or even to 4 per cent., and in the case of inferior oils it may get up to 12 per cent., always supposing the work to be carefully done, for in the opposite case, when much naphtha runs away with the water, the loss may get up to twice or more than that just stated.

The *last operation* is the second alkaline treatment with dilute caustic-soda solution, say, sp. gr. 1·100. This liquor is gradually added during the agitation until a change of colour takes place in the tar-oil, when nothing further is added. Usually the colour changes from reddish brown to light brown or brownish-yellow, and that very abruptly; but sometimes blue or purple colours are observed. Finally, the liquids are well mixed up, and then left for an hour to settle; the caustic liquor is drawn off from the bottom; the naphtha is twice washed with water, and is now ready for distillation. In Lancashire sometimes milk-of-lime is used instead of caustic soda.

The yellowish *colour* of the crude benzol is changed by the action of sulphuric acid on certain of its impurities into a purple, or else into a brown-red shade, but this goes away during the subsequent operation, and gives place to a slightly milky appearance and yellowish-brown colour.

When testing purified naphtha by distillation, the boiling-points are usually found rather higher than those of the unwashed naphtha. This proves that the removal of less volatile bodies (phenols, naphthalene, bases) is more than compensated by that of more volatile ones (methanes, olefines, sulphur compounds). Complete purification, so that nothing but benzene and its homologues remain, cannot be expected; carbon disulphide especially remains, often in very appreciable quantities; and even the "chemically pure" descriptions of benzene, toluene, etc., formerly, till Victor Meyer's discovery of thiophen and its homologues, contained these substances without anybody being aware of it (*cf.* p. 286).

Other Processes for Treating the Light Oil.

Older Processes.—The washing process described above is probably that now generally employed; that is, washing first with alkali, then with sulphuric acid, and again with a little alkali. The employment of the other processes, both those described in our former editions and those to be mentioned below, seems to have been discontinued.

Mansfield used, for every gallon of benzol, ½ lb. of sulphuric acid and 1 oz. of nitric acid of sp. gr. 1·30, sometimes also a little bleaching-powder and hydrochloric acid. For toluene he took ¾ lb. sulphuric and ¼ lb. nitric acid. For the alkaline treatment he employed lime-water or caustic-soda solution. The less volatile hydrocarbons were boiled for five or six hours with a quarter of their volume of caustic-soda solution, sp. gr. 1·30, with reflux of the distillate; the liquid was then distilled and purified by dilute sulphuric, nitric, or hydrochloric acid.

Ronalds and Richardson prescribe treating the light oil twice with sulphuric acid, mixing for several hours, whereby much heat is evolved (probably by excessive action), washing with water, and finally with lime-water or dilute caustic soda. They warn against allowing the light to act upon fresh naphtha, because the water will not readily settle down under the action of light.

Young (quoted in Hofmann's *Report of the Juries*, 1862, p. 140) treats the crude oil with bleaching-powder, gradually adds dilute hydrochloric acid, and at length caustic-soda solution; the oxidized products collect at the bottom as a black layer, from which the clear oil is easily drawn off. In this way the tar from gas-works in which the richer Scottish cannel coals are used is asserted to be advantageously converted into the ordinary products of the paraffin-oil industry [?].

According to Breitenlohner's experiments with peat-tar oils (*Dingl. polyt. J.*, clvii., p. 378), the employment of oxidizing agents, as well as lime in lieu of caustic soda, leads to so much inconvenience, that, after all, sulphuric acid and caustic soda must eventually be resorted to.

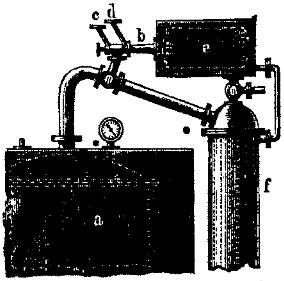

FIG. 186.

H. Hirzel (Ger. P. 34315) combines the distillation of the oils with the chemical washing in one operation, by intimately mixing the vapours of light oil, etc., with the chemicals (acid, caustic liquor) in the state of a spray. In Fig. 186, *a* is the still, *b* the injector (spray-producer), *c* the pipe conveying the steam, *d* that conveying the chemical agents, *e* the preliminary water, *f* the proper condenser.

Fritz Schwarz (Ger. P., 12th March 1904) applies sulphates in addition to sulphuric acid; preferably a mixture of fuming sulphuric acid with sodium or potassium bisulphate.

Glaser and Bürstenbinder (Ger. P., appl. C15062, class 12) apply, after the usual washing with sulphuric acid, another washing with hydrochloric acid, whereby the hydrocarbons are obtained almost entirely devoid of smell.

Nordhausen oil of vitriol is proposed for washing tar-benzols by the Badische Anilin- und Sodafabrik (Ger. Ps. 92018 and 93702). An addition of 4 per cent. of this agent, containing 20 to 25 per cent. free SO_3, is sufficient. This is introduced as a spray into the benzol, kept in agitation, after having first dehydrated the latter by means of ordinary concentrated sulphuric acid (1·84). The apparatus, Fig. 187, consists of a cylindrical case D^3, in which are fixed two concentrical tuyeres D^1 and D^2. Into the inner tuyere D^1 is introduced compressed air or gas, and into the space between D^1 and D^2 the acid to be sprayed. Above the tuyeres the tube D^3 is contracted; the wider orifice F can be closed by cap K; the bottom orifice is

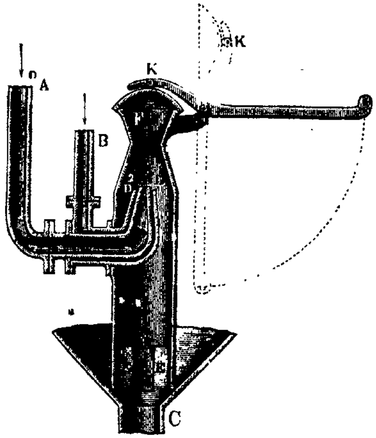

FIG. 187.

provided with slots E for the passage of the liquid. The apparatus is fixed at the lowest point of a tank filled with tar-oil and is started by forcing compressed air or gas through A and D^1, keeping K open, and thus violently pushing the oil upwards through F, other oil entering again at C, so that a circulation is effected. The Nordhausen acid arrives through B, and on contact with the streams of air from D^1 and oil from D^3 it is carried forward, converted into spray and mixed with the oil. When the spraying is finished, K is closed and air is blown in through A and E, to agitate the oil from the bottom. This causes the acid-tar to agglomerate, and to settle rapidly after ceasing the agitation. During the settling cap K prevents the acid-tar from getting into D^3 and stopping up the tuyeres. The apparatus is so constructed that the acid-tar cannot stick fast anywhere, but always runs off. In order to avoid losses through the volatility of benzol, this is agitated by itself, by first filling the agitating-vessel to a height of from 3 to 5 ft. before forcing in the remaining oil (from an elevated tank) together with the sprayed acid. The acid-tar does not act upon cast-iron blowers or pumps, if the surfaces of the moving parts are protected from moisture by petroleum or lubricating oil where they are in contact with the air. The consumption of Nordhausen acid is only about half that of ordinary sulphuric acid, the results are better, and the waste of oil is smaller. After drawing off the acid-tar, the treatment with water and alkali is performed in the usual manner. This process should not be applied to crude, watery oils, but only as a preliminary to separating the *pure* hydrocarbons.

Thiele, Parker, and Fincke (Ger. P. 133426) employ *nitric acid* for the purification of crude benzol. The nitrites and nitro-compounds formed are taken out by finely divided zinc, aluminium, etc., in the presence of caustic alkali, whereby they are reduced to amides.

Walter Feld (Ger. Ps. 202349 and 208190) purifies tar-oils for special purposes by simultaneous treatment with substances containing *sulphur* and other substances which can separate the sulphur from the former (*e.g.*, $2H_2S+SO_2=S_3+2H_2O$). The separated sulphur dissolves in the tar-oil which is recovered by distillation.

Gathmann (Amer. P. 768796) causes during the distillation a current of *hot air* to circulate through the liquid under reduced pressure.

Locality for carrying out the Chemical Treatment of Crude Benzol and Naphtha.—The mixing-apparatus is best fixed in the same room as the steam-stills with their receivers and the receivers of the benzol-still (see below). Considering the great danger from fire, this building should be constructed without any wood, with an iron roof (for instance, one made of corrugated sheet-iron). The roof should be provided with movable ventilators; and the windows ought to possess iron shutters, which can be tightly closed from without with the least possible delay. Open fire (even matches) ought never to be tolerated in this room; it should be lighted by reflectors from without,[1] or by electricity. Inside and outside hydrants and hose should be provided, so that every place may be reached by a jet of water. It has been observed that pure water is not very suitable for putting out fires of light tar-oils, because these float on the top; but *ammonia-water*, which is always at hand at tar-works, does excellent service in this way, probably owing to the volatilization of ammonium carbonate and sulphide;[2] and putting on sand, ashes, and the like acts better than water. The safest plan would be to provide one or more pipes leading from the steam-boiler into the room, through which it could be filled with steam by taps or valves *accessible from the outside;* thus the air would be driven out and the fire quenched; but there must be a large volume of steam, and it must issue in several places all over the room. The doors and windows should be in this case provided with automatically shutting iron dampers which can be worked all together by a single pressure on a knob, or something like that.

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[1] A case has come under my cognizance, and has been described by me (*Dingl. polyt. J.*, vol. cclix., p. 138), where, in a petroleum-refinery, the vapours issuing from a hot still, after the manhole had been taken off, escaped in such quantity that an explosion was caused by their taking fire on a lamp, burning outside the building, at a distance of 20 ft.; the "flashing" caused the fire to be propagated back into the building, which was completely burnt down.

[2] I noticed this many years ago, also in my German work on tar-distilling, published in 1867 (p. 101). Some time later Mr Watson Smith made the same observation, and strongly recommended the use of gas-liquor (to be stored in close tanks and provided with suitable piping and forcing power) for extinguishing fires in cotton-mills Strong ammonia liquor has been also recommended for putting out petroleum fires by a Committee of the Munich Polytechnic Society (*Färber-Zeit.*, No. 26, 1882; *J. Soc. Chem. Ind.*, 1882, p. 351).

For the extinction of fires, *flue gases* (from steam-boilers, etc.) have been frequently recommended, as both their low percentage of oxygen and their contents of carbon dioxide act in this direction. Harker (*J. Soc. Chem. Ind.*, 1915, p. 157) describes an apparatus for that purpose, the principal portion of which is a fan driven by a turbine.

For extinguishing benzine fires *liquid carbon dioxide* has been recommended; this can be blown on to the burning place directly from the iron bottles by means of hose. Carbon dioxide is also used for this purpose in the form of froth produced in a special apparatus (styled "Perkeo" by the inventor) which contains two separately kept solutions; 1st, a solution of sodium bicarbonate, extract of liquorice root, and sodium sulphate; 2nd, potash alum and sodium sulphate. These liquids get mixed before reaching the burning place, where they produce a dense froth and extinguish the flame.

Breslauer (Amer. P. 955316, transferred to the Minimax Co., Ltd., London) extinguishes the flame of burning benzin, etc., by squirting on to it an oxyhaloid of sulphur by means of compressed gases.

If the benzol factory is reasonably laid out and carefully managed, there is no danger of fire, since (according to M. M. Richter) the benzols do not, like petroleum benzin, produce electrical discharges by friction against the insides of tubes and vessels.

On account of the *poisonous* properties of benzols (mentioned *supra*, p. 230), all localities in which benzol is handled must be well lighted, roomy, and well ventilated.

Treatment of the Washed Naphtha.

This can be effected in various ways. Some distil the product at once by steam, as will be described in the next chapter, and collect the distillates as benzol, solvent-naphtha, etc.; others interpose a distillation by direct fire and fractionation. The former process seems at first sight shorter and simpler, but it is advisable only when time presses, since by this plan the last products, especially the burning-naphtha, cannot be kept from discolouring in the course of time. This can be easily prevented by employing the second process, *i.e.*, distilling once more over a direct fire, and making two or three fractions.

This is done in a still exactly like that used for light oil (p. 858); for the sake of cleanliness, it is advisable not to employ the light-oil still itself, but a special *crude-benzol still.* Its worm is made of lead, and, on account of the great volatility of benzol, is rather long. The still and its worm are placed under a shed outside the mixing-house; but the three receivers are either placed inside the house, or at least connected with it by pipes so as to be accessible from within. They consist of well-riveted iron boxes with a manhole and a small hole for running in the distillate from the worm; the latter hole must just fit the pipe, and should be closed by a plug except when in use. This is done both to prevent any loss by volatilization and the danger from fire, since benzene vapours, even very much diluted with air, take fire most readily.

In firing, the same principle is followed as usual—strong firing during the heating up, to be moderated immediately when distillation commences. At first the cooling-water is run as fast as a 1-in. water-pipe will permit, so that the distillate runs off quite cold; only towards the end should it run out tepid.

The fractionation is regulated by a thermometer, which is fixed in the still. This has the drawback that the attendant must be depended upon for changing the receivers at the proper time. But he can be easily controlled by distilling 100 c.c. from a glass retort with thermometer, and noting the quantities passing over at the desired temperatures; according to very many experiments made by myself, the same result is obtained as on the large scale. The volumes thus found are calculated for the quantity put into the still (as measured by an iron gauge-rod in the mixer, or in any other way); and the attendant is instructed to run so many inches' depth into each receiver. If there are tables of the contents of each vessel, the whole, including the calculation, can be done in ten minutes. By this plan a thermometer in the still itself can be dispensed with altogether.

The fixed points of the fractionation will vary according to the desired final products. For 90 per cent. benzol, the first fraction is made at 110°, the second at 140°, the third at 170°, and the still is then stopped. For 50 per cent. benzol two fractions suffice, up to 140° and from 140° to 170°. The second fraction, as we shall see, yields next to nothing distilling below 100°, and therefore serves only for naphtha. It is not advisable to go beyond 170°, as this would injure the quality of the last naphtha; it is better to allow the still to cool overnight, and to work up the residue separately, together with light oil, in order to extract every trace of benzene homologues. The distillation of about 750 gall. lasts eight or nine hours; the still rarely needs cleaning.

The following table gives some idea of the quantities of the products obtained, in percentages by volume of the raw material:—

	Distillate up to 140° (first product).	Distillate from 140° to 170° (second product).	Residue in the still.
First runnings alone	60 to 61	15 to 17	20 to 22
Light-oil naphtha	30 „ 33	40	...
Mixture of both	48 „ 52	22 to 26	...

Utilization of the Waste Acid from washing Tar-oils (Acid-tar).

The specific gravity of the waste acid, when concentrated oil of vitriol has been used to begin with, is about 1·365; and it generally contains as much acid as corresponds to about 45 per cent. rectified oil of vitriol. It is for the tar-distiller the most troublesome waste product imaginable, killing, as it does, all fish in canals, brooks, and rivers, and is perceptible at great distances by its stench and the red colour of the water. Of course the distillers have always incessantly tried to work it up in some way, even without any profit. That this was no easy matter seems proved by the fact that in none of the tar-works visited by me in 1880 had any use been found for this acid, and that it was everywhere allowed to run away or sink into the ground somehow. In any case, it ought first to be neutralized with lime before doing so.

Of course, those tarry substances would do no harm in the cases mentioned on p. 368, where coal-tar is treated by acids for the purpose of converting it into a sort of asphalt, etc. Recently the state of matters has been entirely changed by the uses found for the pyridine bases taken up by the acid-tar; we shall reserve its treatment for this purpose to the close of this chapter, and first deal with the other uses proposed for the acid-tar.

If tar-acid is *diluted* with its own bulk of water, most of the impurities rise to the surface as a tough, tarry substance of most disagreeable smell, and can be skimmed off. This substance does not occupy much bulk, and can be got rid of by burying it in the ground or, wherever the escape of sulphurous acid is of no consequence, by burning. It dissolves in alcohol with a fine red colour, but is insoluble in benzene or naphtha. A patent, taken out by W. P. Jenny in Germany (No. 3577), refers to the vitriol-tar from the washing of petroleum; but if it is at all useful, it must also apply to our case. According to one of his methods, the acid is to be diluted with its own bulk of water; the tarry oil precipitated is to be washed several times with boiling water, and at last with a little soda. It is then distilled up to 250°, and the residue in the retort treated for forty-eight hours with a current of air. The oxygen is absorbed with avidity; and a mass is formed which, after cooling, forms a dark-brown resin. According to the other method, the dirty acid is heated to 100° or 150° for several days, till a sample sinks down in water. It is then poured into water, and the precipitated substance is washed with much water; or else its own bulk of petroleum spirit is first added, in which case the mixture floats at the top. The product is more or less hard, according to its degree of oxidation, and is insoluble in water, alcohol, and alkalis, but soluble in all fats and oils, naphtha, benzene, etc., as well as in the strongest sulphuric acid. Melted up with indiarubber or guttapercha in different proportions, it forms an elastic body which can be used as an insulator; dissolved in light petroleum spirit, it yields a serviceable asphalt varnish.

The dilute acid remaining behind is still red or brown, and disagreeably smelling, as it retains some of the tarry substances, especially all the bases (pyridine, etc.) and sulphonic acids. It has been proposed to employ it for decomposing the phenolate of soda (p. 744); but it is not suitable for this purpose, since besides the colouring-matters, the sulphonic acids and bases would spoil the carbolic acid. It may, however, be used for making superphosphate, and in this case the tarry substances might do some good by protecting roots against insects, etc.; it has been used for this purpose in Scotland (Mennicke, *Z. angew. Chem.*, 1900, p. 1031). Small quantities of that dilute acid can be got rid of by making sulphate of iron or copper.

The Société Oléo-graisse proceeds according to Rave's process (*cf.* Thompson, *J. Soc. Chem. Ind.*, 1888, p. 303). The acid-tar is kneaded with iron, copper, or zinc borings, a little in excess of the quantity required for neutralizing the acids. When that purpose has been effected, the mass is treated with hot water, whereby the sulphates are dissolved and brought to crystallization later on; the melted resins rise to the surface. These, after being well washed with water, have the mechanical properties of *soft asphalt*. This is rendered harder by heating in a still and collecting the naphtha. The remaining asphalt may serve for many of the purposes of natural asphalt; it resembles indiarubber in elasticity, and is sold as "mineral caoutchouc bitumen." A ton of acid-tar furnishes about 10 cwt. of this purified asphalt. If heated further in a still, until only five-tenths remain, the residue forms a mass almost as hard as ebonite, soluble in naphtha—an excellent insulator for electricity, not acted upon by acids and alkalis, and well adapted for electrical insulation as well as for covering acid-tanks. By interrupting the distillation at intermediate stages, different degrees of hardness can be produced. The heated mass can be pressed into moulds, like papier-mâché. If mixed with 40 per cent. sawdust and a little lime and hot-pressed, an excellent fuel is obtained, which burns without melting and with very little ash. On dry distillation, the asphalt is equal to the best coal for the production of gas. By dissolving it in petroleum or naphtha, a good black varnish is obtained which adheres very strongly to metals. When heated in a still, it yields first naphtha, then ($\frac{1}{8}$) light oils, then ($\frac{1}{8}$) heavy oils, similar to the higher paraffins, and in the residue a very hard metallic-looking carbon, which is a good conductor and very suitable for carbon electrodes, etc.

Before Jenny and Rave, Grotowsky had worked the acid-tar from lignite oils for asphalt.

Bengough (Ger. P. 138345) prepares from the acid-tar highly sulphuretted hydrocarbons which can be used for pharmaceutical purposes. When heating the acid-tar with caustic lime, nearly exclusively non-saturated hydrocarbons are formed which combine with chloride of sulphur (S_2Cl_2), yielding viscous, brown, oily substances. Most suitable for this purpose are the higher fractions of the distillate. Thus sulphuretted hydrocarbons are obtained, containing up to 30 per cent. sulphur, which are not identical with the products obtained by means of free sulphur. The latter contain less combined sulphur, have a different smell, and are not so easily convertible by sulphuric acid into sulphonic acids.

Grousilliers (Ger. P. 43900) mixes the acid-tar with sufficient sodium or potassium sulphate to form bisulphate; thereby the impurities separate as a thick tar.

Schwarz and Bauschliger (Ger. P. 46101) expel most of the tar by heating the acid-tar to 150°, allow to cool, add 2 or 3 per cent. of sodium nitrate, and heat slowly to 40° or 80° C. The resinous matters still present are now separated as a carbonaceous crust; the acid is freed from nitric acid by heating.

Veith and Schestopal (*Dingl. polyt. J.*, cclxxix., p. 21) mix acid-tar from petroleum with the waste alkali from the same process and with lime, and work the mixture in a black-ash furnace by the Leblanc process, the resinous matter replacing the coal in this process.

Heinrici (*Z. angew. Chem.*, 1898, p. 525) tried to work acid-tar (from lignite oils) for sulphate of alumina or alum, but without economical success. Decolorizing by kieselguhr was not more fortunate. But success was attained by the following process for manufacturing sulphur or pure sulphuric acid. The acid-tar is mixed with $\frac{1}{8}$ of its weight of lignite-coke and heated in a retort, whereby all the sulphur is given off as SO_2. The gases are first freed from water by cooling, and then passed through washers charged with heavy paraffin oil, where most of the empyreuma is retained. They are then passed through a stoneware pipe filled with lignite-coke, heated to such a temperature that all the SO_2 is reduced to S, but no CS_2 is formed. The sulphur is condensed by cooling, and the CO_2

formed is employed for decomposing the solution of creosote in soda.

Wolniewicz (*Chem. Zeit.*, 1889, p. 1098) dissolves iron, copper, or zinc in the diluted acid-tar, and employs the solution for pickling timber, previously impregnated with resin-soap, whereby metallic resinates are formed, which according to experiments made by Kretzschmar (*ibid.*, 1889, p. 31) have prominent conserving-properties.

Ragosine and Dworkowitsch (Ger. P. 43453) convert the acid-tar into iron salt, and utilize this, by heating, for sulphurous acid and Nordhausen oil of vitriol.

At Young's paraffin works near Edinburgh, the acid-tar was formerly evaporated to dryness and the residue burnt. The sulphuric acid is thus converted into sulphur dioxide, which was utilized in vitriol-chambers. In the great majority of cases no vitriol-chambers are at hand; but the vitriol-tar might still, without dilution (best, perhaps, mixing it with sawdust), be converted into sulphur dioxide by heating in iron vessels, and that compound be utilized for preparing sulphites or hyposulphites (thiosulphates), or for other purposes.

This proposal (made in the first edition of this work) has been strongly recommended by Koehler in the *Chem. Zeit.*, 1885, p. 777. Attention is there drawn to Roessler's proposal for producing cupric sulphate by the action of SO_2 and air upon copper (Ger. P. 22850), and to the employment of SO_2 for decomposing sodium phenolate (*cf.* p. 745). For the last-mentioned purpose the empyreumatic substances are to be removed by washing the gas first with water, then with sulphuric acid, and then passing it through cylinders filled with freshly ignited charcoal. A Körting's injector aspirates the gas and forces it through the solution of sodium phenolate. After separating the carbolic acid, thus set free, from the solution of sodium sulphate, the latter can be reconverted into caustic soda by boiling with lime, and the calcium sulphite formed can serve for evolving more sulphurous acid, while the caustic soda is used over again for extracting the carbolic acid from crude carbolic oil. Thus the soda would not be lost, and the loss of carbolic acid, dissolved or suspended in the solution of sodium sulphate or chloride, as formed in the ordinary process, would be equally avoided.

Stolzenwald (Ger. P. 212000) recovers by gradual heating of the acid-tar all the oils contained therein, and decomposes the remaining resinous and tarry matters by increasing the temperature to about 240°, whereby, according to his statement, most of the sulphuric acid is recovered in such a state of purity that no further decomposition of it takes place even when concentrating it to the highest degree. This is brought about by "boiling elements," consisting of acid-proof cast-iron pipes with alembic, gas-pipe and outlet for the liquid which by means of dampers in the flues are gradually heated more strongly from the bottom to the top, so that at the upper outlet the temperature of 240° is reached. By this process he obtains oils, sulphuric acid, sulphur dioxide, and carbon; the latter remains with the sulphuric acid and is got out by settling or filtration.

Schildhaus and Condera (U.S. P. 956184, *J. Ind. and Eng. Chem.*, 1910, p. 797) carbonize the acid-tar in a retort, with introduction of heated air, and thereby obtain: 1st, a gaseous mixture of SO_2, air, and small quantities of CO_2 and hydrocarbons; 2nd, liquid hydrocarbons; 3rd, coke. The temperature within the retort, as well as that of the air introduced, is preferably kept at 250° to 350°. The acid-tar is run as a thin jet into the retort, which is provided with an endless screw; the escaping gases and vapours are cooled down, the liquefied hydrocarbons are removed, and the remaining gaseous mixture is washed, first by heavy hydrocarbon oils and then by concentrated sulphuric acid, in order to remove all hydrocarbon vapours. There remains in retort a porous, brittle coke which by means of the endless screw is continuously drawn out into a closed chamber.

Precisely the same process is described in the German patent, No. 224566, of the Steaua Romana Petroleum Company. Another German patent, No. 221615, of the same firm describes the manufacture of technically pure sulphuric acid from the acid-tar by running it, either in a dilute state or re-concentrated after dilution, into boiling concentrated sulphuric acid, at the same time passing air through this, and condensing the escaping vapours in suitable receivers to pure sulphuric acid. The presence of concentrated sulphuric acid is only required for the starting of the process. The feeding with black acid is regulated in such manner that the temperature in the pan remains constant.

We can here only refer to the paper of Zaloziecki (*Chem. Rev. Fett-Ind.*, 1898, p. 27), who recommends working the acid-tar for aluminium salts, etc.; and that of H. Frasch (*ibid.*, 1898, p. 28), who recovers organic colouring-matters from the same.

Wedge (*J. Soc. Chem. Ind.*, 1899, p. 345) describes the concentration of dilute waste acid from petroleum-refining by surface heat, by means of oil-burners, followed by distillation in a still, to obtain acid of 66° Bé. Bühler (Ger. P. 287755) describes an apparatus for this purpose.

Wischin (*Z. angew. Chem.*, 1900, p. 507) discusses the proposals made up to that time for dealing with the waste acid in the industry of mineral oils, but without adducing anything new.

A very important use of the waste acid, which at some works permits disposing of it entirely to great advantage, is that for making *sulphate of ammonia.* This has been done to a certain extent for a long time past, and I have myself proposed it in the first edition of this work, employing such acid previously freed from most of the tar by the addition of water. But this makes the acid inconveniently dilute, and most works consequently do not choose to practise it. In the raw state the acid cannot be used directly for the manufacture of sulphate of ammonia, because the nauseous tarry substances would make the latter product unsaleable. There is, however, a way out of this difficulty, which has been utilized at several works for some time, every one of them believing it to be a secret not known to anybody else. By employing vitriol-tar for absorbing ammonia, and carefully skimming off the scum collecting in the ammonia saturators, nearly all the tarry impurities can be removed and a good sulphate obtained. These tarry oils are then worked into the creosote oil or else they are burned; they contain the bases of coal-tar; and these are now to a great extent manufactured in the manner described below.

A very important fact, unknown to most tar-distillers before it was published in a former edition of this work, is the following:—It is well known that sulphuric acid containing any considerable quantity of *arsenic* cannot very well be used in the manufacture of ammonium sulphate, since in that case arsenious sulphide is formed, which discolours the sulphate. For this reason most English ammonia manufacturers used to employ brimstone-acid, although its price is very much higher than that of pyrites acid. But the latter can be used quite as well, if, during the saturating process a certain quantity of vitriol-tar is added to it. The scum formed from the latter carries the arsenious sulphide up to the top, whence it can be skimmed off, and leaves perfectly white sulphate behind. I have seen this done on a very large manufacturing scale at a Dutch works.

A somewhat similar but much more elaborate process for dealing with vitriol-tar is that patented by the Chemische Fabriks Aktien-Gesellschaft in Hamburg (B. P. 9614, 1885; Ger. Ps. 34957 and 36372), which will be described lower down.

According to the Ger. Ps. 289162 and 289524 of the Phœnix A.G. für Bergbau und Hüttenbetrieb, the acid-tar, without dilution, is mixed with ammoniacal liquor and tar-oils or coal-tar, and steam is passed through, thus obtaining on the one hand a highly concentrated ammonium sulphate liquor, fit for immediate working up into commercial sulphate, and on the other hand a tar-product, free from sulphuric acid.

The *examination of acid-tar* for alkyl-sulphonic acids, etc., is performed by Heusler (*Berl. Ber.*, 1895, p. 498) as follows:—The acid-tar is diluted with ice-water, neutralized with lime or baryta, and filtered. The filtrate is decomposed by sodium carbonate, and the filtered solution of the sodium sulphonates evaporated to dryness below the boiling-point. The residue, after dehydrating on the water-bath, is heated with aniline on a paraffin-bath during four hours to 170° C., which process decomposes the sodium alkyl-*sulphates* with regeneration of the hydrocarbons. These, as well as the aniline, are driven off by steam; from the residual sodium *sulphonates* the hydrocarbons can be regenerated in the usual manner.

As a rule it will be sufficient to estimate in acid-tar only the organic substances altogether, which Michel (*Chem. Zeit.*, 1910, p. 1210) does by means of a flask provided with a glass tap-funnel and a gas-delivery pipe. First some saturated solution of potassium permanganate is put into the flask, and then the tar-acid is run in, drop by drop, through the tap-funnel, rinsing this in the end by some pure sulphuric acid and water. After the reaction is finished and the liquid has cooled down, the carbon dioxide formed from the organic substance is found by driving over the gaseous contents of the flask into a gas burette, measuring the volume of the gases, absorbing the CO_2 by caustic-potash solution, and re-measuring. The quantity of carbon corresponding to the CO_2 found may be assumed as expressing that of the originally present organic substance, if increased by one-third.

Recovery of the Pyridine Bases.

These bases have acquired a considerable commercial importance, partly through their employment for the manufacture of colouring matters, for purifying anthracene (*supra*, p. 615), for synthetic purposes, and in some other ways, but principally by the fact that the "denaturation" of spirit of wine in Germany and several other countries takes place by the addition of these bases.

The properties of the pyridine bases have been described on pp. 293 *et seq.*, and reference to their recovery has been already made in the case of carbolic oil, p. 740. But by far the greatest portion of them is obtained from the acid-tar, obtained in purifying crude benzol, and we therefore describe their recovery in this place. First, however, we shall mention some other ways of obtaining them.

Formerly the pyridine bases were almost exclusively obtained in the manufacture of animal charcoal from bones. Both the tar and the ammoniacal liquor formed in this process, when carried out in retorts connected with apparatus for condensing the volatile products, contain those bases, and that in percentages far exceeding those of the coal-tar products. But the quantity of the latter which is at disposal for industrial purposes so immensely exceeds that of the products obtained from bones, that the latter have quite receded into the background. To be sure, coal-tar even now is not the only source of these bases; lignite-tar and especially that from bituminous schists also furnish a considerable proportion of them.

Coal-tar contains only 0·05 or at most 0·1 per cent. of pyridine bases. It is hence practically impossible to obtain these from the raw tar itself, by extracting it with sulphuric acid, as has been proposed. We therefore abstain from repeating here the description of that direct recovery of pyridine from the tar, given in our last edition, pp. 698 *et seq.*

The only practicable way is this: separating the mixture of pyridine bases from those distillates of coal-tar in which it has most abundantly collected, corresponding to its boiling-points. Moreover, it has to be considered, as pointed out by Spilker (*loc. cit.*, p. 78), that the pyridines in coal-tar must be presumed to be loosely combined with phenols, and that it must be very difficult to extract them completely, without having first destroyed those "loose compounds" by the action of stronger alkalis which take hold of the phenols. This is also the reason why pyridine, in spite of its low boiling-point (115°), is found in the higher-boiling distillates; its combinations with phenols have a boiling-point of 180° to 190°. On the other hand it is also found in the first distillates from coal-tar, which pass over far *below* its boiling-point; a mixture of 1 part pyridine with 3 parts water boils constantly at 92° to 95°, and the conditions for the presence of such a mixture do exist in coal-tar (*Berl. Ber.*, 1883, p. 2977). Since the quantity of carbolic oil obtainable from coal-tar (especially coke-oven tar) considerably exceeds that of the "light oil," it can be understood why most of the tar bases accumulates in the last-named fraction.

Some statements respecting the manufacture of the pyridine bases are made by Scheithauer in his book, *Fabrikation der Mineraloele* (Braunschweig, 1895), p. 146. The acid solution, of 15° to 20° Baumé, is freed by long settling from oils floating on the top and resinous matters sinking down, and is filtered through lignite-coke with a little cotton-waste. In the clear solution the percentage of pyridine bases is estimated by decomposing it in a graduated cylinder with caustic-soda solution of 38° Baumé. The quantity generally found in liquids from the working-up of lignite is 20 or 30 per cent. crude pyridine bases. The acid liquid is slightly supersaturated with caustic soda or ammonia, the necessary quantity being ascertained by titration. The process is best carried out by placing the soda or ammonia solutions in a vessel and running in the acid solution of pyridine *bases at the bottom.* Thus the bases are separated quickly and in a pure state; the aqueous solution is run off, the bases are dehydrated by a solution of caustic soda of 38° Baumé, and then distilled. The first 75 per cent. are collected, the temperature having risen to 270° C. This distillate is again dehydrated as before, and is separated into the desired fractions by redistillation in a column-apparatus.

Recovering the Pyridines from the Acid-tar.—Where the manufacture of ammonium, salts is not carried on at the same time with the treatment of coal-tar, but the pyridines are to be recovered from the latter, the chemical washing (*supra*, pp. 869 *et seq.*) must be carried out with a view to this. For this purpose, after extracting the phenols from the light oil and crude naphtha by an alkaline treatment, we must treat the oils first with comparatively weak sulphuric acid, say sp. gr. 1·3, in order to extract the pyridines, without a sulphonating action on hydrocarbons, etc. (p. 869). That weak acid may be quite well prepared from the "acid-tar," p. 887, by diluting it with water up to sp. gr. 1·3, by which proceeding so much of the sulphonated compounds, etc., is precipitated that, after a certain time left for their subsidence, the thin acid, although very strongly coloured, can be employed for the absorption of the pyridines.

We shall now describe the usual treatment of the absorbing-acid for pyridine bases, and we commence with the description found in Muspratt-Bunte's *Chemie*, viii., p. 47 (by Kraemer and Spilker).

The crude "pyridine-sulphuric acid" is a brown-red liquid, strongly acid, of sp. gr. 1·2 to 1·3, and contains from 15 to 30 per cent. of bases. The boiling-points of these differ very much, according to the fraction from which they have been obtained, and range from 100° to 200° C. About half of these is pyridines; in the other half, α-picoline, β-picoline, α-α-lutidine, etc., have been found, also aniline and toluidine. Quinoline and its congeners do not occur in sensible quantity in the acid-tar from crude benzol, on account of their high boiling-points (but naturally that will be different with the waste acid from the treatment of the higher-boiling tar-oils, in which even acridine, etc., will occur). The most valuable portion are the bases boiling up to 140°, as large quantities of these are required for denaturing spirit of wine (in Germany). The small quantity of bases boiling at a higher temperature is mostly employed for the purification of crude anthracene, according to the Ger. P. 42053 (*supra*, p. 615).

Besides the bases, the pyridine acid contains a little benzol and somewhat considerable quantities of rosin-like substances, formed from the tar hydrocarbons, partly dissolved, partly in suspension. These impurities must be removed, as they would pass over into the bases and render these liable to yield turbid solutions. This might be done by concentrating the acid by evaporation and filtering, but it is better done by the process of the Chemische Fabriks-Aktien-Gesellschaft in Hamburg (Ger. Ps. 34947 and 36372), viz., *partial precipitation by ammonia*, as free as possible from water and H_2S, or else by concentrated gas liquor, containing 20 per cent. NH_3. The tar-oils do not contain the bases in the free state; the latter must be first isolated by an alkaline treatment of the oils. The acid-tar is first enriched with bases before being further treated, in the manner following:—The acid-tar is diluted with water to sp. gr. 1·2 or 1·25, which causes most of the resinous matters, etc., to separate at the top as a thick tarry layer. The aqueous acid is rendered quite colourless by agitating with crude carbolic acid, and is then employed for absorbing the bases from crude light oil and carbolic acid, previous to their treatment with concentrated sulphuric acid. The acid solution of the bases is saturated with ammonia in the well-known apparatus for the manufacture of sulphate of ammonia, to be described later on in Part II. This treatment takes place in stoneware pots or lead cylinders, provided with two necks at the top, or a neck at the bottom for a tap and a manhole-lid. The NH_3 gas is passed in by means of a pipe, reaching to the bottom, and this is continued until a sample of the exit-gas smells faintly of pyridine, and the blue reaction on congo paper has just ceased. After a short repose, the contents of the cylinder are found to have separated in two layers. The top layer contains all muddy impurities; the bottom layer is a light yellow solution of pyridine-ammonium sulphate, and is taken to the vessels where the saturation with NH_3 is completed. Two or three such saturators are combined in such manner that all the NH_3 is utilized, the last remainder being retained in a tower fed with pyridine-acid. Here the treatment is continued until a sample shows a distinctly alkaline reaction with litmus. The ammonium-sulphate liquor settles quickly and well. It is run off by the bottom tap into a separating-vessel, fitted with a partition, where the crude pyridine remains in one compartment and the sulphate liquor flows into the other compartment, from which it goes to the evaporating-boxes, and is in all respects treated like the ordinary ammonium sulphate, as will be described in Part II. In this process almost the whole of the acid employed for washing the tar-oils is recovered as sulphate of ammonia, the bases being obtained casually as a by-product. This makes it pay to employ a great excess of acid, to make sure of absorbing all the bases, and to enrich the bases in the liquid by contact with fresh quantities of oil. The yield of bases from coal-tar does not exceed 0·25 per cent.

Distillation of the Crude Pyridine.—The crude pyridine is now distilled in iron apparatus like the light-oil stills (pp. 858 *et seq.*). The first distillate is treated as "first runnings," until it does not contain more than 10 per cent. water. Then comes a middle fraction, as long as a sample, mixed with its own volume, yields a clear solution, and then the "last runnings," as long as any bases come over. The resinous residue in the still is used as fuel. The last runnings are used as a solvent, or for preparing the higher-boiling bases. The first runnings are dried by means of caustic soda in cone-shaped iron vessels, provided half-way over their bottom with a perforated false bottom, on which is placed the solid caustic soda. The caustic liquor formed collects at the bottom, is drawn off, and is employed for a preliminary drying of another charge of first runnings. The dried oil, together with the middle fraction, is redistilled in an ordinary steam-still, such as will be described for benzol (pp. 907 *et seq.*), until a sample of the whole distillate yields 50 per cent. at 140°, and 90 per cent. up to 160°, which is the prescription for denaturing purposes. The small portion remaining in the still is collected until it can be rectified by itself, or else it is treated like the last runnings.

Isolation of the Various Bases.—The following notes on the isolation of the bases contained in coal-tar are due to a private communication from Dr C. Häussermann.

Since there is rarely a sufficient quantity of the mixture of pyridine bases at disposal, which would admit of isolating them by a series of fractional distillations, it is advisable to employ for the preparation of products of constant boiling-points (at least of the lower members of the series) the benzenoid hydrocarbons, isolated by fractional distillation on a manufacturing scale, which are constantly accompanied by those bases. English 50 per cent. and 90 per cent. benzol has always been treated at the tar-works with only a small quantity of sulphuric acid, so that it contains both thiophens and bases. Such benzol, after having been fractionated by a 'Savalle's column into benzene, toluene, and xylene, boiling at a constant temperature, admits the recovery of up to 0·5 per cent. of pure pyridine from toluene, and as much picoline from xylene. If these hydrocarbons are first treated with dilute sulphuric acid, only the bases are extracted, and are at once recovered in the pure state, the fractionation on the large scale having separated the single bases one from another, while thiophen, thiotolen, and thioxen remain behind, and can be extracted by treatment with concentrated sulphuric acid.—Instead of removing aniline from the basic mixture by oxidation, Häussermann prefers to extract it in the shape of aniline sulphate, which is much less soluble than the sulphates of the other bases.

Lessing and Wilton (B. P. 4766, of 1905) *recover pyridine bases from crude ammoniacal liquor* by washing it with heavy tar-oil, or by washing the exit-gases of the ammonia stills, with or without condensation, with a suitable oil, to which preferably a certain quantity of crude cresol is added.

Purification of Pyridine.—At the tar-works as a rule no attempt is made at purifying the pyridine bases otherwise than by fractional distillation. *Aniline* can be removed by cautious addition of fuming nitric acid, gradually heating the liquid up to boiling, then diluting with water, filtering off from any precipitate produced, and saturating the filtrate with caustic alkali. Greville Williams destroys the aniline by diazotizing with potassium nitrite, and hydrochloric acid, followed by heating. The process employed by Häussermann for removing the aniline in the shape of sulphate has been mentioned *supra.*

Pure pyridine as a commercial product can be made from the ordinary denaturing mixture by careful fractionating and drying over caustic potash; if needful, interposing a treatment with potassium permanganate. The product should be entirely free from water, give no reaction with permanganate, and yield at least 90 per cent. on distilling between 115° and 118°.

Analytical Methods for Pyridine Bases.—The mixture of bases recovered from coal-tar consists principally of the bases of the pyridine and quinoline series, together with small quantities of pyrrol and of aromatic bases (aniline, etc.). For technical purposes there is no attempt made at isolating the constituents, and we shall therefore not enter into that question.

Qualitative Testing for Pyridine.—A reaction for pyridine, by means of *a*-dinitro-chlorbenzone, is indicated by Vongerichten (*Ber.*, 1899, p. 2571). Other reactions for distinguishing pyridine from other bases are given by Holdt (*Chem. Zentr.*, 1902, ii., p. 146) and Bräutigam (*ibid.*, ii., p. 166).

Barthe (*Bull. Soc. Chim.*, 1905, p. 659; *Chem. Zentr.*, 1905, ii., p. 259) declares that pure pyridine does *not* turn red litmus blue, as stated in the text-books. He purifies it from ammonia by means of crystals of $MgHPO_4$.

A Test for discovering Denatured Spirits in drinking-brandy has been described by the experts of the German Exchequer as follows:—Evaporate 1 litre of brandy with 1 c.c. concentrated sulphuric acid down to 15 c.c., and add 3 g. solid caustic potash; if pyridine be present, its smell will be perceived at once or after gentle heating. Another test (*Chem. Ind.*, 1900, p. 25) is the addition of potassic-mercurous iodide, which in aqueous solutions gives a yellowish crystalline precipitate with pyridine. Before applying this last, the alcohol must be removed by distillation after adding sulphuric acid. The residue is neutralized with caustic potash, and distilled; the distillate is tested as above. The crystals then formed should give the smell of pyridine when heated with caustic potash.

Quantitative Methods.—Milbauer and Stanek (*Z. anal. Chem.*, 1904, p. 215; *Chem. Zentr.*, 1904, i., p. 1538) describe the quantitative estimation of pyridine bases in the presence of ammonia and aliphatic amines. By adding sodium carbonate to the mixture of salts the ammonia and the amines are converted into carbonates, but the pyridine is set free, whereupon it is shaken out with ether and titrated, using patent blue V. N. as indicator.

K. E. Schulze (*Ber.*, xx., p. 3391) employs ferric chloride for titrating pyridine bases, all other indicators being useless. Five c.c. of the bases is dissolved in 100 c.c. water, and 1 c.c. of a 5 per cent. ferric chloride solution is added. Ferric hydrate is thereby separated in a flocculent state, and normal sulphuric acid is cautiously added until the precipitate has just dissolved.

A test for the proportion of pyridines suitable for *denaturing purposes* is their conversion into the cadmium-chloride compound. The bases separated by caustic soda are distilled with the caustic liquor, until the drops coming over do not any more show the taste of pyridine. The distillate is mixed with four times its volume of absolute alcohol, measured, and 10 c.c. of the liquid is mixed with 50 c.c. absolute alcohol and 2 c.c. of a concentrated aqueous solution of cadmium chloride. After standing for twenty-four hours the white crystals which have appeared are collected on a tared filter and dried at 100° C. One hundred parts of these correspond to 46 parts of pyridine bases (Kraemer and Spilker).

The following directions have been issued by the German Federal Council for the qualities to be possessed by the *pyridine bases employed for denaturing spirit of wine* (*alcohol*). The mixture should be colourless or slightly yellow, and contain not more than 10 per cent. water. At 140° C. and 760 mm. pressure 90 per cent. ought to distil over. A later order, of 9th March 1905, indicates 160° C. as the temperature up to which 90 per cent. should distil over; this means a considerably greater facility for manufacturing the bases, since now the lutidines and collidines are usable as well. The bases should be miscible with water in all proportions without essential turbidity, and free from ammonia. After standing for some time the colour ought not to be deeper than that of a mixture of 2 c.c. normal iodine solution + 98 c.c. water. Ten c.c. of an aqueous 1 per cent. solution, on being shaken with 5 c.c. of a 5 per cent. solution of cadmium-chloride, should within ten minutes yield a distinctly crystalline white precipitate. Ten c.c. of the 1 per cent. solution should give a white precipitate with 5 c.c. of Nessler's reagent. Twenty c.c. of the basic mixture, combined with 40 c.c. of water, should separate no oil-drops. On shaking 20 c.c. of the bases with 20 c.c. of caustic-soda solution, sp. gr. 1·4, and settling, the mixture should yield at least 18·5 c.c. of bases. One c.c. dissolved in 10 c.c. water should not require less than 9·5 c.c. of normal sulphuric acid, until a drop causes a distinctly blue margin on congo-red paper, which soon vanishes.

According to the directions given above, the 20 c.c. denaturing mixture, on being mixed with its own volume of caustic-soda solution, sp. gr. 1·4, should yield 18·5 c.c. of bases and contain 9 per cent. of water. In order to estimate the percentage of water more exactly, shake 100 c.c. of the bases in a stoppered 150 c.c. cylinder with fused caustic potash, in pieces of the size of peas, until after thorough settling the volume of the top layer does not any more decrease and the bottom layer shows a considerable quantity of undissolved potash. Read off at the same temperature as the bases had before the operation; the diminution of volume then indicates the percentage of water.

Malatesta and Germain (*Boll. chim. farm.*, 1913, liii., p. 225; *J. Soc. Chem. Ind.*, 1914, p. 1198) found this test to give good results only if solutions of high alcohol concentrations (at least 90 per cent.) be used, and the formula: $CdCl_2,C_5H_5N$, be accepted for the double compound.

The estimation of pyridine in *ammoniacal liquor* is described in Vol. II. under that heading.

Applications of the Pyridine Bases.—By far the most important application of these bases is that for denaturing the spirits of wine, intended for technical purposes, so as to make the spirits unfit for consumption as drink. In 1903 436 tons of pyridine bases was used in Germany for this purpose. For the following fiscal years the quantities used were:—

Fiscal year.	Pyridine used.	For denaturing alcohols.	Fiscal year.	Pyridine used.	For denaturing alcohols.
	Tons.	Litres.		Tons.	Litres.
1903 to 1904 .	469·4	478,998	1907 to 1908 .	534·5	545,343
1904 to 1905 .	417·6	426,180	1908 to 1909 .	473·4	485,011
1905 to 1906 .	481·4	491,184	1909 to 1910 .	725·4	740,224
1906 to 1907 .	408·5	416,347	1910 to 1911 .	491·7	501,769

The use of pyridine bases for denaturing alcohol has also been sanctioned in the United States (*Asph. and Teerind. Zeit.*

1907, p. 68). They are to be employed in the proportion of 0·5 parts, together with 2 parts methylic alcohol, on 100 spirits. The quality of the bases is to be tested as in the German prescriptions (quoted *supra*, p. 902).

Further uses of pyridine are mentioned in the following publications:—

The Berliner Holzkontor, in 1900, applied for three patents for preparations of pyridine for disinfecting and preserving purposes (Ger. Ps. appl. B25537, 26664, 26665).

According to Merck's *Jahresber.*, 1902, p. 144, pyridine, in dilutions of 1:750 and 1:350, kills Bacterium coli. It is medically employed as a solvent for uric acid, against dipsomania, against whooping-cough, for protecting animals against horse-flies.

Wohl (Ger. P. 139669) promotes the esterification of cellulose by acetyl chloride by the addition of pyridine and quinoline bases.

The Farbenfabriken vorm. Bayer (Ger. P. 145238) convert nitroanthraquinone by heating with pyridine into oxyanthraquinone.

Synthetic indigo is purified by means of pyridine (Höchster Farbwerke, Ger. P. 134139; Compagnie Parisienne des Couleurs d'Aniline, Fr. P. 314681).

Pyridine forms extremely reactive compounds with carbonyl chloride, according to several patents taken out in 1900, 1901, and so on.

Kahlenberg (*Z. angew. Chem.*, 1901, p. 148) applies it in the preparation of lithion.

Trachmann (*Pharm. Zeit.*, 1902, p. 470) proposed employing pyridine for taking the carbon disulphide out of coal-gas. Bueb reports on experiments made with this process as having been unsuccessful (*J. Gasbeleucht.*, 1903, p. 736).

Frank (*ibid.*, p. 491) recommends for the same purpose a special mixture containing high-boiling tar bases with benzol, a little aniline, and a little free sulphur.

Pyridine is used by Merck (Ger. Ps. 90308 and 104664) for preparing piperidine by electrolysis; for the preparation of basic diazo-colours by the Farbwerke vorm. Meister, Lucius and Brüning (Ger. P. 105202), for various other synthetical processes in the industry of colours and of pharmaceutical preparations, for the extinction of the phylloxera, for some analytical processes, etc.

Other Bases.—M'Kenzie (*J. Ind. Eng. Chem.*, 1909, i., p. 360) states that from the ordinary mixture of bases by fractional distillation at 134 to 134·5 *picoline* can be obtained which is very superior to pyridine as a solvent for indiarubber, and in some respects even better than disulphide of carbon.

Quinoline is the starting-point for a synthesis of indigo by the Comp. Paris. des Couleurs d'Aniline (Fr. P. 314681). Decher and Kopp (*Ber.*, 1906, p. 72) for this purpose oxidize its addition-product with chloro-acetic ester by heating with permanganate, filtering, adding alkali, evaporating, and heating to 200°.

Isoquinoline, according to the Ger. P. 285666 of the Gesellschaft für Teerverwertung Duisburg-Meiderich, is obtained from crude quinoline by partial saturation or partial precipitation from the acid solution, or fractional extraction, utilizing in all these cases the more strongly basic properties of isoquinoline in comparison with quinoline.

Coumarone-resin.

This is obtained, according to the Ger. Ps. 270993 and 281432 of Wendriner, from heavy benzol, boiling at 160° to 180°, by treating it with 0·25 per cent. of concentrated sulphuric acid, running this in in a thin stream, and cooling the benzol, so that the temperature does not rise above 120°. If the tar-acids and bases have not been previously removed, about 0·5 per cent. of sulphuric acid must be used, and the resin is not so pure. Precautions must be taken to avoid overheating of the resin when distilling off the solvent-naphtha.

CHAPTER IX

CARBOLIC OIL (MIDDLE OIL)

FOR some years after the preparation of carbolic acid became an industry it was found suitable not to work for that purpose the whole of the "light oil," but merely the last portion (that between sp. gr. 0·980 or 0·990 and 1·000). Since then the demand for carbolic acid as well as that for naphthalene has arisen to a considerable extent. Consequently all the principal factories manage their process so as to obtain a special fraction between that yielding the light hydrocarbons and the heavy oils, which is particularly rich in phenols and naphthalene, and which is called "Middle Oil" or "Carbolic Oil." We have seen (pp. 448 *et seq.*) that this fraction is not made everywhere exactly on the same principles; and its quality at one works will consequently differ a good deal from that at another; but this makes no difference in the manner of treating it to the best purpose, which we shall describe *infra.*

Carbolic oil, if quite fluid, *i.e.*, at about 40°, such as it is obtained in the first distillation of coke-tar, generally from 7 to 8 per cent. of the total distillates, has a yellow up to light-brown colour, and smells distinctly both like carbolic acid and naphthalene. Its specific gravity, taken at 40° and calculated for 15°, is not below 1·000, on the average = 1·02. At ordinary temperatures it is semi-solid or pasty, owing to the presence of naphthalene, of which about 25 to 30 per cent. crystallize out when the oil cools down.

In Muspratt-Stohmann's *Chemie*, 3rd ed., vi., p. 1179, the composition of middle oils is stated as follows:—

Distilling at	I.	II.	
100°	0	0	per cent.
100° to 180°	14·1	9·2	„
180° „ 200°	41·5	35·2	„
200° „ 250°	38·7	19·2	„

Watson Smith gives the following results for "light oils, really equal to "middle oils" from Wigan cannel-coal tar:—

Distilling below	Oil of sp. gr. 1·000.	Oil of sp. gr. 1·019.
170°	10	0 per cent.
180°	5	0 "
190°	12	5 "
200°	22	24 "
	49	29

Middle oil (carbolic oil) contains up to 40 per cent. naphthalene; from 25 to 35 per cent. phenols (one-third of this being phenol proper = carbolic acid, and two-thirds the three cresols with a little xylenol); further, the two methyl-naphthalenes, and about 5 per cent. bases, principally pyridine, quinoline, and quinaldine. The striking circumstance that pyridine, the boiling-point of which is = 115°, is found in considerable proportions in that oil, boiling at much higher temperatures, is explained by Spilker as being due to its combining with phenols, and in this form boiling only at 180° to 190°. That compound is only split up on treating the oil with caustic-soda solution; therefore the extraction of the bases can only be performed after removing the phenols by caustic-soda solution.

The fraction collected as carbolic oil is run into tanks, where it is allowed to cool down, whereupon 25 or 30 per cent. naphthalene crystallize out, from which the liquid oil is separated in the usual way. This oil is a very thin liquid, of sp. gr. 0·99 to 1·01; it contains from 25 to 30 per cent. phenols, from 15 to 25 per cent. (according to the temperature) of naphthalene, and a little of the methylnaphthalenes and other compounds mentioned on p. 648 as found in the creosote oil. It possesses a characteristic "carbolic" smell.

Small tar-works usually sell the carbolic oil as such; others partially work it up into varnishes. Larger works manufacture from it at least crude carbolic acid, if they do not proceed as far as the pure article.

The *working-up* of the carbolic oil is carried out differently in different factories. Either the crude oil is put into cooling-tanks, in order to get out the naphthalene, whereupon both the oil drained from the naphthalene and the naphthalene itself are redistilled, or the crude oil is distilled as it is, without waiting for the naphthalene to crystallize out.

According to Rispler (*loc. cit.*) the first of these processes cannot be carried out with every description of middle oil. Such as is obtained from gas-tar contains up to 25 per cent. of acid oils, which keep a great portion of the companions of naphthalene in solution; the naphthalene crystallizing out is coarse-grained, and can go directly to the presses to be worked up. But the middle oil from coke-oven tar contains only 13 per cent. of acid oils, which low percentage is not sufficient for keeping the companions of naphthalene in solution; hence the latter separates in small crystals, is of a spongy nature, includes much liquid oil, and to a great extent passes through the presses. Since the treatment of the middle oil in the cooling-house and the presses requires much manual labour, increasing with the higher percentage of oil, it will be preferred in most cases to begin with a fractional distillation of the middle oil, all the more as the expense of getting out good naphthalene in that way is only one-third of the cost of pressing. Moreover, the crude middle oil of course contains part of the constituents of the first fraction, the light oil, which causes losses by evaporation during the treatment of the warm middle oil in open vessels. We therefore in this place describe only the second process, which differs from the first only by the different sequence of the single operations.

Redistillation of the Carbolic Oil.

This is carried out in stills, heated by a direct coal-fire, and constructed exactly like a tar-still, holding from 5 to 20 tons. Sometimes they are provided with a dephlegmating-head 3 to 6 ft. high, which simplifies the ulterior separation. The work is carried on like the first distillation of the tar itself, but is much easier, as no boiling-over need be apprehended, and lasts from twenty to twenty-four hours. At first a little crude benzol, say 6 or 7 cwt., comes over, together with the hydration-water of carbolic acid. When this is finished, the distillate is turned into the second receiver. The next period, during which the distillate should run in a jet about as thick as an ordinary lead-pencil, lasts six or eight hours, and about 3½ cwt. of water comes along with the oil. During this period the heating must be carefully regulated, to prevent boiling-over through a sudden liberation of hydration-water. When no more water comes over, all danger is passed, and the distillation can be carried on vigorously. Up to this moment the distillate is regarded as crude benzol and treated as such, as we shall see in the next chapter.

From this point the distillate is collected for carbolic acid, until a sample on cooling on a glass-plate shows a crystallization of naphthalene, at which point the thermometer indicates 215° or 220° C. This period lasts nearly ten hours, and yields about 55 cwt. oil.

At most works the distillation is now interrupted and the residue run into the creosote-oil tank. At some places another fraction is taken, containing no more crystallizable phenols, but 40 or 50 per cent. cresols, which, after separating the naphthalene, is sent out as 40 to 50 per cent. carbolic acid, or else worked up into creoline or lysol (pp. 658 and 660). The residue from this can be employed merely for softening the pitch.

According to E. Waller,[1] in America the light oil is distilled at temperatures below 177° to 220°; steam is passed through the distillate so long as it carries away any oils; the distillate ("rectified coal-tar naphtha") is worked for benzol, and the residue ("naphtha tailings") for phenol. If these short hints actually represent the American style of treating the first coal-tar fractions, it cannot be pronounced as quite rational. Formerly it was frequently held that the distillation of the tar-oils, especially of the lighter and non-viscous descriptions, from stills heated by ordinary fireplaces, was more dangerous than that of the tar itself, because in case of leaky places in the seams the thin oils more easily get to a place where they can take fire. But that fear has no foundation; such small quantities of oil are immediately burnt without any danger; and where the distillation is carried out under diminished pressure, no leakages at all will occur. Therefore it has been recommended to carry out the rectification of the creosote oil by means of a steam-coil, but this is certainly only exceptionally done.

Sometimes the creosote-oil stills are provided, not merely with a dephlegmating-head, as mentioned *supra*, but with a large dephlegmating-column, of which there are a great many descriptions in use for many purposes, wherefore we need not go into particulars about them. These columns are made of wrought-iron or cast-iron, not of bronze, which is not merely much more expensive, but would be acted upon by the sulphur compounds of the tar-oils.

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[1] *Chem. News*, xliii., p. 150.

The *fractions* usually made in this distillation are as follows:—

1. *Crude benzol* up to the boiling-point 165° or the sp. gr. 1·00. This fraction is worked up, together with the similar product obtained in the working-up of the light oil (*vide infra*).

2. *Carbolic-acid oil* up to the boiling-point 195° or sp. gr. 1·005. This is worked up principally for phenol and naphthalene, together with the analogous fractions obtained from creosote oil and light oil.

3. *Naphthalene oil* up to the boiling-point 220° or the sp. gr. 1·025. Worked up in an analogous way.

4. *Residue* remaining in the still; *vide supra*, Chapter VIII.

At the same as crude benzol (fraction No. 1), a little *water* passes over, formed from the phenol hydrates. As long as this is the case, the distillation must be carried on very cautiously. As a rule the change should be made for the next fraction (carbolic-acid oil) at the point when no more water comes over, and when the rattling noise in the still (caused by condensed water getting into the hot oil) has ceased. Now the distillation may be hastened by putting more fuel on to the fire-grate.

It is unnecessary to say that the fractionation is carried out in various ways at different works Thus Rispler (*loc. cit.*) gives the following data:—

Distillates.	Middle oil from gas-tar.	Middle oil from coke-oven tar.
	Per cent.	Per cent.
Up to 165°: Crude benzol	4·15	1·78
Up to 199°: Carbolic-acid oil	21·77	19·91
Up to 220°: Naphthalene oil	43·45	28·68
Residue	26·91	48·18
Water and loss	3·72	1·45
	100·00	100·00

The fractions obtained as above have the following general properties:—

Carbolic-acid oil has the sp. gr. 1·000 to 1·005, a smell similar to that of middle oil, and at ordinary temperatures it forms a thin paste, owing to the secretion of naphthalene. It boils from 160° to 250°. This fraction contains about 25 to 40 per cent. phenols, and about as much naphthalene, one-third of which remains in solution after cooling; also about 7 per cent. of bases. Among the phenols, phenol proper ($C_6H_5.OH$) is present in larger proportion than the cresols.

Naphthalene oil I boils between 180° and 230°. On cooling down, about 40 per cent. of nearly pure naphthalene crystallize out and are separated from the liquid portion by pressing. This fraction, moreover, contains about 15 per cent. of acid oils, and up to 3 per cent. bases.

Naphthalene oil II is that which is got from creosote oil (*vide supra*, p. 650). It boils between 200° and 280°, and on cooling equally separates much solid raw naphthalene which, however, contains acenaphthen, methyl naphthalene, and must be redistilled (*vide* p. 832). It contains also acid oils (homologues of cresol), hydronaphthalene, diphenyl, quinoline bases, etc.

Whichever way the fractionation is carried out, the further work is conducted in a similar manner to obtain the following products:—*Crystallized carbolic acid, cresols, heavy solvent naphtha, pyridine bases, and naphthalene.* We shall consider these *seriatim.*

E. Barbet et Fils et Cie. (Fr. P. 473082) obtain the 2 per cent. benzol, contained in heavy oils, in one distillation in a column distilling apparatus, where the oil is first distilled by heating coils supplied with high-pressure steam; and the naphthalene is then separated by the injection of low-pressure superheated steam.

Obtaining Naphthalene by cooling down the Carbolic Oil.

The greater portion of the naphthalene can be removed from this oil by cooling it down. The *cooling-boxes*, made of sheet-iron, are usually placed in a common cooling-house in tiers one above the other. Below these there are the *draining-boxes*, made of galvanized undular iron, placed in a slanting position, so that the liquid oils may run down to the holes provided for getting them out, into boxes from which they get into the montejus, by means of which they are delivered to the places for working them up.

The inclined bottom of the draining-boxes is covered by a grating, made of triangular laths of wood, which facilitates the running away of the liquid oils.

The *cooling-house* must have ample dimensions, so as to give sufficient time to the oil for cooling down, and must also be constructed in such a way that the carbolic-acid oil and the naphthalene oils can be kept separate for their further treatment.

The size of the cooling-boxes must be adapted to the quantity of the oil produced *per diem*, so that each box can be completely filled in one operation. It should be avoided to fill up partially filled boxes with fresh oil after the crystallization has commenced, since this would not merely disturb the crystallization, but moreover the hard crust, formed at the top of the first portion of oil interferes with the running-off of the new portion. Rispler recommends in lieu of large boxes, to employ a considerable number of small boxes, as these cool down more quickly.

In some places it has been attempted to reduce the pretty considerable expense for manual labour in this operation, by effecting the cooling of the oil and the separation of the solid and liquid portion by *mechanical agitating apparatus*, but this proved to be less economical than the ordinary working of the cooling-houses.

The oils draining from the cooled-down naphthalene oil are as a rule *final products.* From *naphthalene* oil I is obtained *crude commercial carbolic acid* (*vide infra*) containing from 25 to 30 per cent. tar-acids, and by repeated fractionation products, richer in these acids. From naphthalene oil II is obtained a *creosoting-oil*, which is mixed with the same quantity of anthracene oil, in order to serve as *pickling-oil* for the impregnation of railway sleepers, telegraph poles, etc. (*vide supra*, pp. 679 *et seq.*).

On the other hand the *carbolic-acid oil* drained from the naphthalene is usually fractionated once more, so that the principal fraction boils between 160° to 205°, and contains about 35 to 40 per cent. acid oils. These are taken out by treating the oil with dilute caustic-soda solution, followed by taking out the bases by dilute sulphuric acid, and the further treatment for phenols, cresols, and pyridine bases described *infra*.

Manufacture of Carbolic Acid and of Cresols.

Experience has shown that carbolic acid proper (C_6H_6O) cannot very well be made from the creosote oils distilling above 240°. These always contain phenols, but mostly the higher homologues; and the latter are universally admitted to be of great importance in the process of preserving timber, being less soluble in water, and less volatile than carbolic and cresylic acids, so that it would seem wrong to remove them. We shall therefore not take the heavy oils into account for the manufacture of carbolic acid. On the other hand, if a "middle oil" has not been collected (from about 170°) in the working-up of the "light oil" (to be described in the next chapter), considerable quantities of residues rich in phenol and naphthalene are obtained; these are added to the "carbolic oil," and make it about equal to the "middle oil" of other works.

The first treatment of the rectified carbolic oil aims at the separation of the phenols from the indifferent hydrocarbons. The process originally proposed by Laurent[1] is essentially identical in principle with that which is employed at the present time. The fraction of coal-tar distilling between 150° and 200° is treated with a hot saturated solution of *caustic potash or soda*, some solid powdered caustic potash or soda is added, and the mixture well agitated. [In this detail, viz., employing solid caustic, the process differs from that at present in use; probably at the time when Laurent published his process, in 1831, the tar did not contain so much naphthalene as now, because the cast-iron gas-retorts then used could not be worked at such a heat as those now made of fireclay; moreover, Laurent worked with a comparatively low-boiling fraction, poor in naphthalene.] The oil sets to a crystalline paste; the liquid portion is decanted, and the solid part is dissolved in warm water. Two layers are formed—one light and oily (which is removed), the other heavy and watery (which is saturated with sulphuric or hydrochloric acid). The oil which is formed in the latter process and found floating upon the acid liquid is digested with fused chloride of calcium and fractionally distilled. Thus a white oily substance is easily obtained, which on being slowly cooled yields beautiful crystals.

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[1] *Ann. Chim. Phys.* [3], iii., p. 95.

It has been attempted to cheapen Laurent's process by employing lime[1] in lieu of potash or soda, boiling and strongly agitating. On settling, the neutral oils come to the surface and are removed by decantation; the lime-precipitate is decomposed by hydrochloric acid, and yields phenol. This simple and cheap process, however, does not give a good result; and the treatment with caustic soda is universally preferred, but with a much weaker solution than that prescribed by Laurent. At all events the preparation of perfectly pure crystallized carbolic acid is anything but simple and easy. It is said that such acid was first made on a large scale by Sell, of Offenbach;[2] but in any case it was introduced into trade on a manufacturing scale through the exertions of Crace Calvert and Charles Lowe, of Manchester, who for a considerable time had almost a monopoly of it. At the present day it is made at other English as well as Continental works.

First of all it should be ascertained how much *alkali* the oil requires. It is not necessary in this case to make a formal analytical estimation (of which we shall speak hereafter), but only to find the minimum quantity of alkali required for exhausting the oil. This need only be tested for roughly, in the following manner:—50 c.c. of the oil is put into a 100 c.c. graduated cylinder; and soda solution is gradually added, shaking after each addition and allowing the liquids to separate. The dark-brown solution of sodium phenolate is distinct from the oil which may be above or below it. The volume of the oil is noted; and if on the next addition of alkali it is not lessened, the last addition must have been sufficient. From this is calculated the quantity of alkali to be used in actual manufacturing work.

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[1] *Cf.* Hugo Müller, *Z. f. Chem.*, 1868, p. 270 (Runge had done this from the first).

[2] According to a private communication from Mr Brönner, of Frankfort, this gentleman as early as 1846 made so-called white limpid ("wasserhelles") creosote, which was frequently refused because in winter it solidified to a white crystalline mass! This was, of course, owing to the then general confusion between carbolic acid and the real, original "creosote" from beech-wood tar, which latter compound is never found in the solid state.

From what we have seen (pp. 273 *et seq.*) respecting the behaviour of phenol and cresol with alkalis, we know, first, that the lowest phenol, C_6H_5OH, that is, "carbolic acid" proper, is more easily soluble than its homologues, and hence requires a weaker lye; secondly, that a large excess of caustic liquor may reprecipitate the phenols. Still the margin is so large, that in regular manufacturing work a test like that just described is hardly required, because there will be no very striking differences in the percentage of phenol. But where unknown oils have to be treated, such a test will have to be applied.

Fractional Saturation.—According to Behrens (*Dingl. polyt. J.*, ccviii., p. 363) an important manufacturing "secret" for making crystallized carbolic acid consists in treating the oil with a quantity of dilute soda solution, insufficient for dissolving all the tar-acids; in that case carbolic acid, being the strongest, is first taken up. This is confirmed by G. E. Davis (*J. Soc. Chem. Ind.*, 1893, p. 233), who treated light oil three times in succession with one-third of the proper quantity of caustic-soda solution of 1·010, and who obtained crystallized phenol only from the first and second extraction, and nothing but cresols from the third.

It would appear (*e.g.*, from Kraemer and Spilker, in Muspratt-Bunte's *Chemie*, viii., p. 52; Spilker, *Kokerei und Teerprodukte der Steinkohle*, p. 80) that this fractional saturation, which utilizes the greater affinity of phenol proper to caustic soda, in comparison with the cresols, is also practised at several Continental works, *e.g.*, in this manner. They analyse their crude oils and add to them only so much caustic liquor that it takes up nearly all the carbolic acid and but little of cresols (say, from 40 to 75 per cent. of the total quantity of alkali required for saturating the acids in the carbolic oil, *vide supra*); when acidified, it yields crude carbolic acid solidifying at 25° to 30° C. The oils separated from the sodium carbolate solution are now treated with enough caustic-soda solution to extract the higher homologues of phenol, and the last remaining oil goes to the creosote-oil tank, or to the light-oil still.

The following special prescription for the extraction of phenol was given by Charles Lowe, the first manufacturer of the purest crystallized carbolic acid (Allen's *Commercial Organic Analysis*, 1st ed., p. 305): 20 tons of gas-tar are introduced into a retort and distilled. The first 200 gall. of "light benzols" are of no use for the extraction of carbolic acid. When that amount of distillate has passed over, the next 600 gall. are collected separately. For each 200 gall. of these oils, having a density of 1·0 to 1·005, 30 gall. of caustic-soda solution of sp. gr. 1·34 are added after dilution to 150 gall., and the oils are then agitated with the solution for two hours. The mixture is next allowed to settle for four hours, when the alkaline solution is drawn off and neutralized with sulphuric acid. The crude carbolic acid rises to the surface and is skimmed off, and is then allowed to settle in tanks for several days, after which it is ready for casking. The caustic soda used must be free from nitrates.

Here, as we see, rather dilute alkaline liquor is prescribed. In regard to this, the following points should be borne in mind:—The less pure the oils, the weaker should be the caustic solution, if good phenol is aimed at. With crude benzol (which always contains some phenol) stronger caustic can be employed; and the phenol obtained will be still better, though less in quantity, than that from carbolic oil. For this reason some distillers do not begin the washing of crude benzol, as usual, with sulphuric acid, but with caustic-soda solution of sp. gr. about 1·200. In the case of "middle" or carbolic oil, such strong alkali would dissolve too much hydrocarbons, especially naphthalene, which would greatly impede the purification of carbolic acid, and might altogether prevent it from crystallizing. Moreover, oils are dissolved which have a tendency to turn dark in the air, and thus spoil the phenol. Hence in this case weak alkaline liquors must be employed; and probably Lowe's prescription is more trustworthy than any other, since his object is to obtain the best quality of crude carbolic acid from the tar-distillers.

Watson Smith takes 33 per cent. by volume of caustic liquor 18° or 19° Tw. for carbolic oil, or 40 per cent. by volume for light oil.

At a large English factory carbolic acid is extracted from all the light distillates, up to (of course not including) creosote oil, in the following manner:—The first runnings are treated with rather stronger caustic-soda solution, viz., of sp. gr. 1·15, and in great excess. This is done previous to the washing with vitriol. The solution thus obtained, containing some carbolic acid along with much free soda, is mixed with a fresh quantity of somewhat weaker alkali, so that the specific gravity descends to 1·125. This liquor is now employed for treating the carbolic oil, at a temperature of 65° to 77° C. The resulting solution of carbolate of soda is separated from the naphthalene oil floating on the top, and the latter dissolves also the impurities taken up by the caustic soda from the first runnings, which otherwise cause the carbolic acid, made from first runnings alone, to be of inferior quality. Thus, by simplifying the process, both the quantity and the quality of the carbolic acid are improved.

A large South German manufacturer states (in a private communication to the author) that he obtains crude carbolic acid (with 50 per cent. crystallizable acid) by employing caustic liquor of sp. gr. 1·26, steaming the solution, and decomposing the alkaline liquor by acid. He lays much stress upon the subsequent fractional distillation of the crude acid, but none upon the employment of weak alkaline liquor, or upon fractional saturation.

Kraemer and Spilker (*vide supra*) employ for the present purpose a solution of sodium hydrate of sp. gr. 1·1, containing 100 g. NaOH per litre, which takes up about 250 g. of the mixture of phenols and cresols per litre.

Where only crude carbolic acid is aimed at and no special conditions are imposed by the buyers, sometimes stronger alkaline liquors, up to sp. gr. 1·32, are employed; but this must yield a product difficult to refine.

As we see from these notes, the concentration of the solutions of sodium hydrate employed for the purpose in question varies in pretty wide limits in different factories.

Formerly, when the carbolic acid was set free from the solutions of phenolates by the addition of strong mineral acids (sulphuric acid), whereby the caustic alkali previously employed was practically lost, attempts were made to replace it by cheaper agents.

Knights and Gall (B. P. 5824, of 1887) agitate carbolic or middle oil with a mixture of *cream of lime and solution of sodium sulphate.* On settling, two layers are formed, the lower one being a solution of sodium phenolate in water, which is run off. The top layer consists of tar-oil, calcium sulphate, and a little solution of phenols; after passing through a filter-press, some more of the phenol-sodium solution can be separated. The latter is decomposed with sulphuric acid, and the sodium sulphate formed is used over again as before. In lieu of lime, any other alkaline earth, and in lieu of sodium sulphate, potassium sulphate can be used.

Staveley (*J. Soc. Chem. Ind.*, 1888, p. 807) proposes a similar process for the manufacture of sodium or potassium phenolate from the sulphates or sulphites, and states that, especially when employing phenols free from hydrocarbons, up to 96 per cent. of the sulphate or sulphite can be decomposed. He slakes about 11 cwt. of quicklime, and makes it into about 2 tons of cream of lime. When this is nearly cold, about 20 cwt. of phenols, boiling between 190° and 250°, or a corresponding quantity of tar-oil, is added. The mixture is slowly run into a warm solution of 30 cwt. of sodium sulphate in about 4 tons of water, contained in a heatable pan provided with an agitator. The temperature of this mixture is kept at 30° or 40°, and the agitation is continued for an hour after finishing the addition of the calcium phenolate. After the mixture has settled down, 70 or 75 per cent. of the sodium phenolate solution can be got by decantation. The remainder is passed through a filter-press or a vacuum-filter, the residue is washed with about 3 tons of water, and the washings employed in the next operation as a solvent for sodium sulphate. If tar-oil is employed in lieu of distilled phenols, a certain portion of the oil and of the phenolate is retained by the gypsum. — The solution of sodium phenolate is thoroughly carbonated with lime-kiln gases, and the phenols which separate out are run off after a few hours' settling. The solution of sodium carbonate, containing about 1 per cent. phenols, can be evaporated and the soda-ash calcined as usual. In order to recover that small quantity of phenol, a corresponding quantity of caustic-soda solution may be added before the evaporation. In this case the phenol accumulates in the mother-liquor, which is again added at the close of a new operation, to avoid the presence of free caustic lime, which impedes the settling.

The same process, but extended to di- and trioxybenzene, oxynaphthalenes, and dioxyanthraquinones, has been patented by Landshoff and Meyer (Ger. P. 48270). They state that the reaction takes place most easily with alkaline sulphites, less quickly with the sodium sulphate, and still more slowly with potassium sulphate.

The Chemische Fabrik Ladenburg (Ger. P. 147999) also proposed hydrated lime for separating the phenols from the neutral oils. To a ton of tar-oil, containing about 200 up to 210 kg. phenols, 56 kg. of lime, in the shape of a 10 per cent. milk of lime, is added, thoroughly mixed, and the liquid allowed to rest. The solution of calcium phenolates, after being separated from the neutral oils, is heated at reduced pressure at 60° to 65°, until no more oils distil off. The clear solution of the phenolates is either drawn off and decomposed by strong mineral acids, or the distillation is continued at ordinary pressure and by the aid of superheated steam, whereby half of the phenols is driven off, basic calcium phenolate remaining behind. The latter is either likewise decomposed by a strong acid (of which, of course, the same quantity will be required as had been previously used for driving off half of the phenols), or it is united with the distilled aqueous liquid after separation from the phenols, and employed for a fresh extraction, having regard to the fact that the formation of a neutral salt requires only 1 mol. of lime to 2 mol. phenols, but 2 mol. of basic calcium phenolate. (This patent was abandoned in 1906.)

We do not know whether any of these processes are anywhere employed in actual practice. Probably the great majority of works employ Laurent's process, with the modifications above described.

The mixing of carbolic oil and alkaline liquid must of course be done very thoroughly. It seems to be indifferent whether the mixture is made at the ordinary temperature or after heating, say to 40° or 50°, by means of a steam-coil or steam-jacket, except in the case of oils containing a large proportion of naphthalene, which should be treated after warming up, in order to avoid the separation of naphthalene in the solid state. Probably all larger works employ mechanical means for mixing. At some it is done by pumping both liquids continuously backwards and forwards, from a lower tank into a higher one and *vice* *versa.* At others they employ horizontal cylinders covered by a bad heat-conductor, with a longitudinal shaft and agitating-blades. Horizontal agitating-shafts have the drawback that they must pass through the sides of the vessel in stuffing-boxes; but the agitation caused by them is more thorough than that produced by vertical apparatus. One of the best forms of the latter is that of a perforated piston moving up and down, as described by Hübner, in *Dingl. polyt. J.*, cxlvi., p. 421. We shall treat of mechanical mixers more in detail in the 11th Chapter. At some places the agitation is effected by blowing in a current of air, divided by a cross of pipes with many holes, or a perforated plate. This principle has the advantage of dispensing with all working parts within the liquid, and thus being equally applicable for acids and alkalis; the blowing can be performed by the same small blowing-engine which is employed at most tar-works for pumping the liquids by air-pressure, but it is asserted that the carbolic acid extracted in this manner, owing to the action of the air, is more inclined to reddening than otherwise. Fig. 165 shows this arrangement. *a* is a perforated false bottom, which serves for dividing the current of air blown in through *b*, into numerous jets; *c*, manhole; *d*, funnel and tap for charging with oil and alkali; *e*, steam-coil; *f*, discharge-cock a little above the bottom; *g*, another discharge-cock in the bottom itself. The air-blast must be so regulated that the liquid shall not be splashed about, but only made to well up thoroughly. Instead of employing a plain cylinder, as shown here, it seems preferable to make the bottom cone-shaped, or to give to the whole vessel the form of a truncated cone, at the lowest part of which the inlet pipes for air and steam are situated. A detailed paper on the application of compressed air for the pumping and mixing of liquids has been published by Ramdohr (*Dingl. polyt. J.*, ccxvi., p. 158).

According to Watson Smith, the oil and alkali are mixed up for an hour and a half; the mixture is then tested by mixing, in a 200 c.c. graduated cylinder, 140 c.c. of the alkaline liquor with 14 c.c. strong sulphuric acid, and allowing it to subside; unless at least 10 or 12 per cent. crude carbolic acid is found to collect at the top, the mixing should be continued.

The mixing-vessel for this purpose is always made of iron, usually wrought-iron, which metal resists the liquor better than any other; the steam-coils, air-pipes, etc., are also made of iron. When mixing by an air-blast, the vessel should be only two-thirds full, on account of the frothing up. It is mostly closed by a wooden or iron cover, to minimize volatilization. According to the size of the works, the settling (which occupies several hours) either takes place in the same vessel, or else the whole contents are run into a special vessel, placed at a lower level, so that the mixer can be charged again at once. The settling-tank must have two (iron) discharge-cocks, one in the bottom itself, another in the side a little above the bottom. The unchanged oil always floats on the alkaline liquid, which sometimes doubles its bulk and is of intensely dark brown colour. First of all this liquid is run off by the bottom cock, which is closed as soon as any traces of oil appear. Now the upper cock

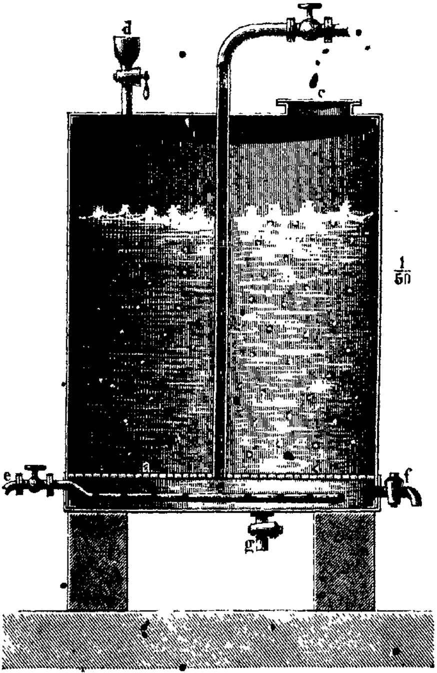

Fig. 165.

is opened, through which oil entirely free from alkali can be drawn off, whilst between the two cocks a layer of both liquids remains, which is best left behind in the vessel and worked up with the next charge. This is facilitated by making the bottom of a conical shape.

As stated by Watson Smith, the point at which the alkaline liquid is going to change for the oily one can be safely recognized by the turbid, milky appearance which sets in.

It is imperative to keep the alkaline liquid as pure as possible from the separated crude naphtha, because even a small admixture of the latter (especially of the naphthalene contained therein) afterwards prevents the crystallization of the carbolic acid. Hence great care must be taken in settling and in drawing off.

The *oil drawn off from the solution of sodium phenolate* (crude naphtha) contains some of the higher homologues of benzene and naphthalene (according to K. E. Schulze, *Berl. Ber.*, 1887, p. 409, 15 per cent. trimethylbenzenes, 15 or 20 per cent. tetramethylbenzenes, 15 or 20 naphthalene, and a paraffin melting at 20° C.), with pyridine bases. It furnishes principally naphthalene, pyridine bases, and solvent naphtha of various degrees. If naphthalene is not wanted, this oil is usually run to the "light oil" (*cf.* next chapter) and worked up therewith. Sometimes this does not pay, viz., when the original oil has been collected later on in the distillation; then the residues are put into the creosote oil. Where naphthalene is to be manufactured, this oil is by far the best raw material for it, as we shall see below.

This oil was formerly frequently redistilled, and the fraction coming over till 180° was worked for *solvent naphtha*, of which 90 per cent. distils between 120° and 160°. Since the recovery of benzol from coke-oven gases has been very much extended (*vide supra*, p. 70 *et seq.*), large quantities of oils boiling between 160° and 200° are required, free from phenols and naphthalene; and this has caused another process for working-up the above-mentioned oils, in which the *pyridine bases* are ~~also~~ recovered, as will be described in Chapter X. In this place we only mention what can be done with the oil remaining behind in that process, by working it for *absorbing oil*, as used for recovering benzene from coke-oven gases.

After the bases have been extracted from the carbolic oil, it is sometimes treated with quite dilute caustic-soda solution before being redistilled in a light-oil still, with a thermometer. It can serve as an absorbent for coke-oven benzene without being washed with concentrated sulphuric acid, as it need not be colourless. The first runnings, say up to 160° or 170°, are combined with a corresponding fraction of the light oil (*cf.* next chapter), and after chemical washing mainly yield ordinary solvent naphtha (120° to 160°) with a little "absorbing oil." The next fraction is collected up to 215° or 220°, and on distilling in a glass flask shows the desired boiling-points (90 per cent. passing over between 160° and 200°). At first it is but slightly yellow; on being kept for some time it turns darker. The residue in the still goes to the creosote oil.

The same oil also contains benzonitrile or sodium benzoate formed from this (*cf.* pp. 266, 306), and can be treated for the recovery of *benzoic acid* as described in the patent of the Aktien-Gesellschaft für Teer- und Erdöl-Industrie, Ger. P. 109122. It is heated in an iron boiler with caustic-soda liquor of sp. gr. 1·4, as long as any ammonia is given off. On cooling the residue separates into an aqueous and an oily portion. The former is saturated with CO_2, the phenols separating thereby are removed, and the residue is now a pure solution of sodium benzoate, from which benzoic acid is obtained as a precipitate of fine white crystals by adding some stronger acid. On cooling down, the whole liquid forms a crystallized paste of benzoic acid which is saleable in this state, and after re-crystallization or sublimation yields an excellent description of benzoic acid for pharmaceutical and other purposes, since it is absolutely free from chlorine compounds.

Treatment of the Liquor containing Sodium Phenolate (Carbolate)

This liquor, to which is regularly added that obtained in the washing of benzol and light oil, may be at once decomposed by acid. But it is usually preferred to interpose a special treatment for the *removal of impurities.* Thus Vincent (quoted by Payen, *Précis de Chimie Industrielle*, 6th ed., ii., p. 961) adds to the liquor five or six times its bulk of boiling water, to precipitate the dissolved hydrocarbons. This should not be overdone; and anyhow the success of this operation will depend upon the fact whether more or less concentrated alkali has been employed from the first. (Vincent starts with concentrated alkali.) Schnitzler (*Dingl. polyt. J.*, ccxiv., p. 86) recommends, as extremely efficient, heating the dark liquid in a copper still over a strong fire till the distillate (consisting of water, naphthalene, oils, and phenol) turns milky; the thermometer will then stand at 170°. Most of the phenol remains with the soda as a mass solidifying on cooling. It is dissolved in water in the still itself, and is diluted to three times the original bulk. After some days a mud is deposited, from which the clear liquor is separated. The latter is decomposed by dilute sulphuric acid; and the phenol separated is distilled from a glass retort. After putting aside the water coming over at first, colourless liquid phenol of honey-like (?) smell was obtained, which solidified on the addition of a small piece of calcium chloride, or a crystal of carbolic acid. The portions passing over last were faintly yellow, and contained more liquid parts. The crystals, after draining them by means of a Bunsen pump and pressing them between paper, remained white for months in a stoppered bottle in moderate daylight; in an open glass they soon turned pink, and at last deliquesced to a yellow-red liquid. The colour was evidently produced by particles of dust floating in the air (? see below).

For the large scale Schnitzler recommends a wrought-iron still with a block-tin, lead, or copper worm, and to put a second delivery-tube lower down for use in the later stage of distillation. Insufficiently heated sodium carbolate yields yellow, unpleasantly smelling phenol; it is essential to completely remove the colouring impurities by evaporation or carbonization, etc. An experiment with calcium carbonate did not succeed (perhaps because there was an excess of lime); the mass turned spongy, conducted the heat badly, and retained tarry matters and naphthalene.

Another purifying process is described in Stohmann-Kerl's *Chemistry* (3rd ed., vi., p. 1181). The crude sodium carbolate is run into open wood tubs, on the bottoms of which is laid a steam-coil perforated with many holes. The liquor is moderately warmed; and enough freshly prepared cream of lime is added to make the whole milky white. During this operation the mass is worked up with a wooden rake, and the heating is continued for twelve hours. After a few hours a skin appears on the surface, which gradually turns into a red foamy scum. This consists of the naphthalene left in the liquor, mixed with lime. It is carefully removed with a perforated wooden scoop, either at once, or at least after the liquor has cooled down. Thus all naphthalene, even to the last trace, can be removed; but it is most essential to keep the heat at the right point. The temperature must never rise so high that the liquid wells up strongly. Perhaps an insoluble compound of lime and naphthalene is formed; but the action of the lime may be only mechanical, the naphthalene being secreted from the alkaline liquor as it is diluted by the steam blown in. In any case the tubs must be left uncovered and must stand in a cool room. When the naphthalene has been completely removed and the liquor has settled, it is carefully drawn off from the lime remaining at the bottom, and is decomposed by sulphuric acid.

The following process is now generally employed for the previous purification of the liquor:—It seems to be efficient and indispensable for obtaining good crude carbolic acid (free from dissolved or finely suspended hydrocarbons, a very slight admixture of which afterwards impedes the crystallization of phenol) that a current of *steam* is passed into the liquid, contained in an iron still provided with a refrigerator, till a sample of the distillate is perfectly clear and bright, without any milkiness.

The stills employed for this purpose are usually old steam-boilers or tar-stills, of a capacity of 5 tons and upwards, provided with a fire-grate and an open steam-pipe, as well as a cooling-worm for the vapours. At first they are heated by an open fire, until the distillate is entirely free from oil, but even after several days' firing the water coming over has still a disagreeable smell. This is removed by finishing the operation by blowing in direct steam during six hours; before doing this, the manhole is opened, so that the steam escapes into the air.

The solution of sodium carbolate in the still is now a dark liquid, entirely soluble in water, except a few floating solid particles, consisting of empyreumatic substances, which must be removed by filtration before separating out the carbolic acid. The only distillate collected during the operation is worked for

we shall see.

Now follows the *decomposition of the alkaline solution of phenols by mineral acid, and the separation of crude carbolic acid.* This operation is generally performed in a wooden vessel lined with lead, which may be provided with a mechanical agitator; but in this case mixing by hand is easy and simple. Kraemer and Spilker (*supra*, p. 733) state that iron vessels may be employed, as the reaction is first alkaline, then neutral; but lead-lined vessels are preferable, as in this case a slight excess of acid does no harm. Sometimes this tank is covered over, so that any noxious gases escaping in decomposing the sodium phenolate by acids can be conveyed under a fire and burned. The acid employed for the decomposition is mostly *sulphuric acid.* The solution of sodium sulphate resulting from this is probably never utilized as such; and the spontaneously crystallizing Glauber's salt is also of very small value.[1] If dilute caustic liquor and sulphuric acid of 140° Tw. be employed, but little will crystallize out spontaneously. Some tar-distillers take strong oil of vitriol (sp. gr. 1·84); but this is worse than useless, as sulphophenols are formed, which in the subsequent distillation decompose and carry sulphurous acid into the carbolic acid. The addition of the sulphuric acid must be cautiously made, to avoid strong heating, and is continued till the reaction has become distinctly acid. The men can tell this from the change of colour, without applying litmus-paper. According to Watson Smith, 1000 gall., treated with 400 gall. of caustic-soda solution of sp. gr. 1·090, require about 22½ gall. of sulphuric acid of sp. gr. 1·74.

It has been several times attempted to replace sulphuric acid by the "acid-tar," formed in washing the light tar-oils (Chapter XI.), after depriving it, by dilution with water, of most of its tarry parts. But it is still very impure; and its use for decomposing sodium phenolate has been given up everywhere, as the saving of acid does not compensate for the contamination of the phenol. It is true that another motive for this procedure was the desire to get rid of that acid refuse; but the proposal of E. Kopp, to combine the employment of this refuse acid for decomposing the sodium phenolate with working-up the resulting solution for the bases contained in coal-tar, could hardly be expected to meet with success, looking at the deterioration of the carbolic acid. We shall see in the next chapter that this "acid-tar" is now generally worked up for the recovery of the pyridine bases.

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[1] According to Watson Smith, the crystals always turn blue on standing in the air.

According to Watson Smith, in Lancashire at his time even fresh sulphuric acid made from pyrites was not employed for this purpose, but almost exclusively acid made from Sicilian brimstone. [This was probably done in consequence of an unfounded prejudice; for the reason, given in the *J. Soc. Chem. Ind.*, 1882, p. 342, that pyrites acid discolours the sodium sulphate, cannot hold good here, as the value of the crystallized sodium sulphate is very slight, and certainly much less than the difference in price between pyrites acid and brimstone acid; moreover the sodium-sulphate solution is nearly always run to waste.] He further mentions that attempts had been made, but unsuccessfully, to replace sulphuric acid by *hydrochloric acid*, which is cheaper [and causes less trouble by crystallizing salts]. The alleged reason of this failure is that chlorides of ammonium and organic bases are formed, which later on are decomposed, and action upon the iron of the stills ensues; the ferric chloride distils over, and makes the carbolic acid dark and dirty. Ammonium sulphate produces no such consequences. [Against these statements must be placed the fact that some of the best German works employ hydrochloric acid, and among them are those that turn out the very finest quality of white crystallized carbolic acid.]

Lowe and Gill (B. P. 1453, of 1880) propose decomposing the alkaline phenol solution by *sulphurous acid*. The aqueous solution of the bisulphite formed in this operation is either to be evaporated for crystallization, or employed for preparing sulphurous acid again. The sulphurous acid would be obtained very cheaply by working-up the "acid-tar" from the washing of crude naphtha (*cf.* this in Chapter X.). But H. Köhler (*Carbol-säure*, etc., 1891, p. 33) has shown that no saleable bisulphite can be made in this way, since the SO_2 from "acid-tar" is too much contaminated with empyreumatic substances. Moreover, the "acid-tar" is more advantageously employed for recovering the pyridine bases. But he found, at least in the laboratory, that the SO_2 can be purified by suitable means, such as adding sulphuric acid, creosote oil, wood charcoal, etc., before passing it into the solution of sodium phenolate, by means of a Körting's injector. The solution of sodium sulphite thus formed might be decomposed by caustic lime (a process described in Gutzkow's Amer. P. 198293), thus recovering caustic soda, and calcium sulphite, to be used as such or for the recovery of SO_2. This process might also be combined with that of Knights and Gall (p. 735), by employing the sodium sulphite solution, mixed with caustic lime, for the extraction of fresh quantities of carbolic acid.

Köhler (*loc. cit.*) found that *nitre-cake* (acid sodium sulphate, with about 30 per cent. free SO_3) can be very well employed for decomposing the sodium phenolate, either in solution or in the state of fine powder. This is especially advantageous where calcined sodium sulphate (salt-cake) can be cheaply made from the crude Glauber's salt crystallizing out in the process.

In the place of strong acids, *carbonic acid* can be employed for decomposing sodium phenolate. In Scotland this process seems to have been used for some years;[1] Brönner,[2] of Frankfort, had previously used it many years ago. A patent has been taken out by Clift (B. P. 967, of 1880) and another by Wischin (B. P. 3750, of 1880) for this process, which is nowadays probably employed in most well-equipped factories.

The carbon dioxide used for this purpose need not be anything like as pure as that required for other purposes, *e.g.*, for making soda by the ammonia process. It is quite sufficient to make it by the action of limestone and coke (not coal; for of course the CO_2 must be free from bituminous substances) in a cupola furnace, and purifying the gas from dust and also from SO_2. This can be done by passing the gases through a shaft filled with lumps of limestone, kept moist by a current of water. Since, anyhow, a pump is used for moving the current of gases, there is no difficulty in this process. The purified gas, which is under a pressure of ¼ to ½ atmosphere, is now passed into the sodium carbolate liquor by means of a perforated pipe lying at the bottom of the tank.

If the decomposition can really be completed without wasting too much carbonic acid, which is achieved by employing two or three vessels in succession, so that up to 90 per cent.

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[1] Mills, *Destructive Distillation*, p. 17.

[2] Private communication to the author.

of the CO_2 is utilized, there are considerable advantages gained by this process as against the employment of strong acids. In the former case the soda is not lost, as in the latter, but is recovered as carbonate and can be used over again after causticizing. There would not, as now, be a rather considerable amount of phenol lost, either dissolved or suspended in small drops, in the solution of sodium sulphate or chloride; for as the liquor is causticized and used again, the phenol would be recovered. No washing of the phenol would be at all necessary, as the latter would retain no mineral acids, which probably give rise to the formation of traces of rosolic acid (p. 280), and thus turn the carbolic acid red.[1] This, of course, presupposes that the carbonic acid itself should be entirely free from stronger acids, which is hardly the case in the ordinary way of working, since even the CO_2 made from coke or in lime-kilns is contaminated with sulphurous acid. It seems therefore necessary to wash the carbon dioxide most thoroughly with water, or else to produce it by the action of superheated steam on limestone in iron retorts. Lest too much of it should be wasted, it should be divided into numerous jets by a perforated false bottom or the like, and several vessels should be employed in rotation to utilize the gas methodically, so that the fresh gas (which in the case of lime-kiln gases contains upwards of 30 per cent. CO_2 by volume) is always brought into contact with nearly saturated liquor, and the poorest gas with fresh liquor, on the same principle as that in accordance with which black ash is lixiviated.[2] There would also be this advantage, that, as the carbonic acid need not in this case be free from oxygen, any fire-gases might be used, if well washed; oxygen even acts advantageously here (*vide infra*).

According to Spilker (*loc. cit.*, p. 81), the treatment of 500 tons phenol-cresol mixture per annum requires the carbonic acid produced by a lime-kiln of 2·3 to 5 ft. diameter, and 10 to

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[1] According to Dr Kraemer (priv. comm.) the reddening of phenol is caused by benzoic acid, contained in the crude phenol, which passes over in the distillation and takes up some iron from the cooler. The ferrous salt thus formed is converted into ferric salt by the oxygen of air, and this produces the red colour.

[2] This is described in detail in my treatise on the *Manufacture of Sulphuric Acid and Alkali* (Gurney & Jackson), 3rd ed., vol. iii., 1911, pp. 300 *et seq.*

16 ft. high, provided with an outside sheet-iron covering for keeping the brickwork together and keeping the air out. If the kiln is properly built and carefully attended to, the charge should be 4 limestone to 1 coke. The less coke is consumed. the richer in CO_2 will the gases be, which are aspirated from the upper part of the kiln below the charging-funnel by an air-pump or exhauster, and carried away with a plus-pressure of about ¼ atmosphere. Before entering into the air-pump or exhauster, they pass through an air-cooler and a washing-tower, about 15 ft. high and 2 ft. 6 in. wide, filled with limestone, over which so much water trickles down that the temperature of the gases going away from it is about 40° or 50°.

J. Hardman (B. P. 7079, of 1885) runs the alkaline solution of the phenols down a coke tower, in which ascends impure carbon dioxide, namely, the gases from the manufacture of ammonium sulphate, after having been freed from sulphide of hydrogen by oxide of iron. The inventor also utilizes the suggestion (already mentioned in the first edition of this treatise, 1882) to recausticize the alkaline carbonate formed, and thus to save the 2 or 3 per cent. of tar-acids otherwise lost with the sodium-sulphate liquors. According to G. E. Davis (*J. Soc. Chem. Ind.*, 1893, p. 233) this process was then regularly in use at Hardman's works.

W. Mason (*J. Gas Lighting*, 1910, p. 947) recommends as a source of CO_2 [which has been utilized for a great many purposes for many years!] the waste gases from the manufacture of sulphate of ammonia, after cooling, washing, and taking out the hydrogen sulphide by means of ferric oxide. According to him, if a reflux-cooler is interposed between the column for driving out the NH_3 and the saturator, by which means the H_2S is kept out, the gases issuing from the saturator are nearly free from moisture, so that there is no cooler and washer required for them [which seems very doubtful!]. In *Met. Chem. Engin.*, 1915, p. 293, Mason gives some details on this process.

Köhler (*loc. cit.*) has introduced into the manufacture of carbolic acid as a cheap source of carbon dioxide the crude bicarbonate prepared in the manufacture of ammonia-soda, which is put into the hot, steamed-out solution of sodium phenolate, with vigorous agitation. The concentrated solution of sodium carbonate, formed in this process, is cooled down for crystallization, the crystals are calcined, and the mother-liquor is causticized, in order to serve again for the extraction of phenols. By this means he obtained phenol of blameless smell. It should, however, be noted that this process can only pay when there is a good price obtainable for the crystallized sodium carbonate.

Some experiments made in my laboratory (*Chem. Zeit.*, 1883, p. 29) seem to show that the separation of phenol from its salts by means of carbonic acid is complete. It may also be stated that difficulties which formerly caused some manufacturers to abandon this process, after trying it for a while, have been overcome, and it can be recommended without any hesitation.

Sulphuretted hydrogen has also been proposed for decomposing the carbolate of soda (Jane, Elland, and Steuart, B. P. 2469, 1883). Since the patent was annulled, owing to the neglect of filing the final specification, there does not seem to be much in it.

After the separation of the crude carbolic acid, the solution of *sodium sulphate*, if sulphuric acid has been employed, must be drawn off hot, lest it crystallize in the precipitating tank. If hydrochloric acid had been employed for decomposing the sodium phenolate, there is no such danger, and more time can be given for the solutions to clear, so that less phenol is lost with the solution of salt. The latter is drawn off by a tap in the bottom, which is shut the moment any carbolic acid appears, whereupon the latter can be drawn off in the pure state from another tap higher up. It is preferable to leave the carbolic acid to itself for a day or two to clear, so that the salt solution suspended in it may completely separate at the bottom: this can be done in a special settler. The longer the time given for the salt solution to separate from the carbolic acid, the better for the quality of the latter.

Working up the Crude Carbolic Acid.[1]

Crude carbolic acid has a specific gravity, varying with its contents of water from 1·05 to 1·065 at 15°, and is essentially a mixture of phenol with the three isomeric cresols and xylenol.

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[1] Much of the following is taken from H. Köhler, *Carbolsäure und Carbolsäure-präparate*, Berlin, 1891.

It should not contain any neutral tar-oils, naphthalene, etc. We shall later on describe the methods for examining it.

In many cases the crude carbolic acid is now sold as such; in other cases it is *washed* once or twice with water, with addition of a little sodium carbonate, in order to remove the mineral acids—which, however, is never done completely, because the washings would carry away too much carbolic acid. In any case the washings should not be thrown away, but employed for dissolving the caustic soda. The washings are found floating on the top of the carbolic acid, and are run off best by a drop-syphon (Fig. 166), which can be gradually turned down. This is much more convenient than a common siphon.

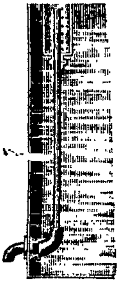

FIG. 166.

According to Spilker (*loc. cit.*, p. 81) the quantity of water (or sulphate-of-soda solution) contained in crude phenol is about 15 per cent., that of the cresols about 10 per cent.; it can be diminished by adding a little solution of sodium bisulphate or sulphuric acid of 60° B., thorough stirring, and drawing off the heavy salt solution accumulating at the bottom.

Bickerdike (*Chem. News*, xvi., p. 168) recommended for the same purpose the addition of 1 or 2 per cent. of dehydrated cupric sulphate, but on the large scale the water is simply removed during the various redistillations.

The *waste-water* running away in carbolic acid manufactures generally contains traces of that acid, which are very troublesome when that water gets into a public water-course; even its treatment with lime does not quite remove the smell. Weigelt and Mehring (*Chem. Ind.*, 1904, p. 596) propose effecting this by treating the waste-water with ozonized air, but this is probably too expensive in ordinary circumstances.

Manufacture of Pure Carbolic Acid

The *first distillation of crude carbolic acid* has merely the object of removing the water and the residue from the principal fraction. The water goes away almost entirely at 100°, whereupon the boiling-point rises rapidly, and at 180° anhydrous phenol passes over. This distillation is effected in stills (Fig. 167), holding up to 10 or 15 tons, made of cast- or wrought-iron and not too high. They are heated from without, with a curtain-arch protecting them against the direct flame. A thermometer is fixed in such a manner that its bulb is at the level of the still-head and the scale is outside. In this first distillation the cooling-worm may be of iron. In distilling, the first fraction consists of everything coming over below 180°; this is mostly water, with hydrocarbons separating out above and some phenol, which is recovered later on. The second fraction, between 180° and 205°, is allowed to crystallize; it goes up to the point where a sample of the distillate yields no more crystallizable products. A third fraction is made up to 220°. The residue is either at once run to the creosote oils, or else it is again distilled with a coal-fire or with open steam, in order to yield liquid carbolic acid (*i.e.*, cresols). In the latter case the last residue is of the nature of soft pitch, and is used as such.

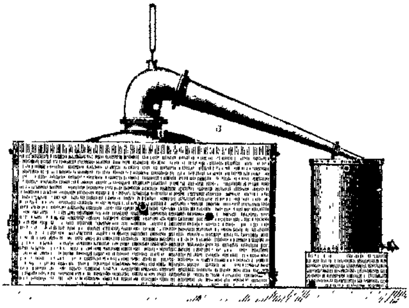

FIG. 167.

It is of the greatest importance not to work too rapidly, as the phenol cannot be separated from the cresols if the operation is hastened. Up to the end of the second fraction the distillate should not run in a jet of greater thickness than an ordinary lead-pencil; afterwards the fire may be increased. The time occupied for a 15-ton still should be from twenty-four to twenty-eight hours. A skilled workman can manage without a thermometer.

The third fraction is redistilled in the same apparatus. It yields, of course, no aqueous first runnings, and only very little of the oils distilling up to 205°, but principally the fraction passing over between 205° and 220°, and small quantities of residue which is worked up as described *supra*. This fraction contains principally the three cresols, but also considerable quantities of crystallizable phenol—just as the fractions up to 205°, although they crystallize on cooling, are strongly contaminated with cresols.

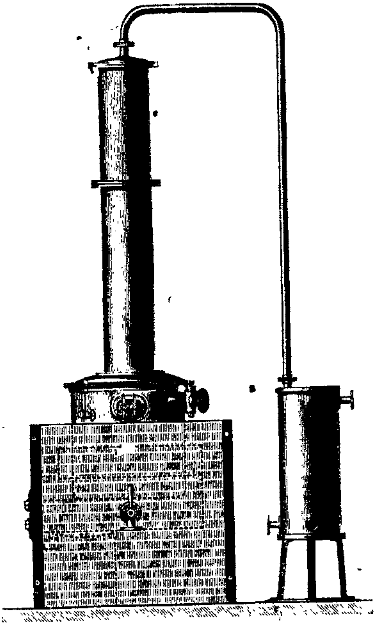

FIG. 168.

If the distillation is carried on very slowly, it is unnecessary to employ stills with a column-head like that shown in Fig. 168, which, however, is preferred by some manufacturers. Another apparatus, by which phenol is said to be completely separated from its homologues, is shown in Fig. 169. Three or four stills, placed in a row, are simultaneously charged with crude carbolic acid. They are heated by means of coal-fires or by steam-coils; the first of these must receive superheated steam. The heating commences in each at the same time; the last stills are stopped when their contents are at 80° C. The heating of the first still is continued, and the vapours given off by it suffice for distilling the contents of the following stills. By this process, it is stated, the last still yields a product crystallizing at once and ready for use.

We can understand the fractionating action of this apparatus, but we doubt whether phenol obtained from it by a rough distillation will fulfil the present requirements of the trade for crystallized carbolic acid.

According to Marzell (*Chem. News*, xxxviii., p. 105), some English manufacturers employ the apparatus constructed by Gifard and Delaire for the separation of aniline and toluidine,

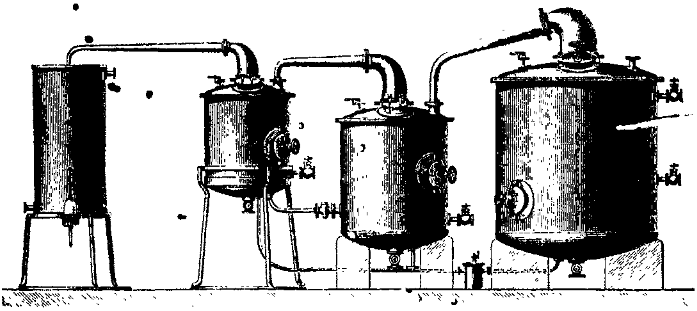

FIG. 169.

which must also be suitable for phenols, as their boiling-points very nearly agree with those of the amides. In Fig. 170, *g* represents a still with discharge-pipe (*t*), manhole (*h*), thermometer, vapour delivery-pipe (*a*), and a pipe (*b*) for running back the liquid that comes from the separator (*k*). This separator, formed of lead pipes, is placed in a trough (*i*) filled with pure phenol or with oil or paraffin, heated by a separate fire and covered by a lid in which is fixed a thermometer and a pipe (*d*) which, when phenol is employed, leads to a worm (*r′*) or, in the case of oil or paraffin, into a chimney. The separator itself is connected by *f* with another worm (*r*).

When the still *g* is fired, the vapours pass into *k*, and heat the contents of *i* to the boiling-point of phenol. This is hastened by first heating up *i* nearly to that point. The phenol vapour given off in *i* is condensed in the worm *r′*. The vapours passing

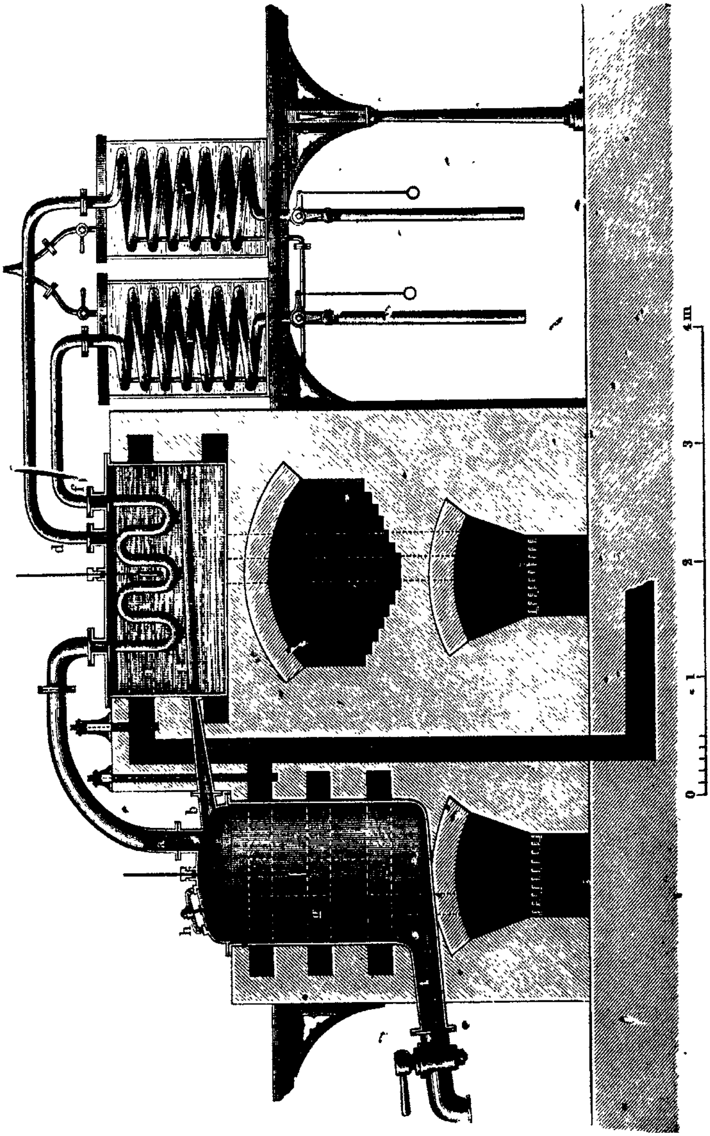

FIG. 170.

through the bends of *k* are here separated into a liquid portion, essentially cresol, which collects below in *e* and runs back to *g*, and vapour of pure phenol, which condenses in *r*. When all the phenol has passed over, the cresol, if required, can likewise be obtained pure, *i.e.*, free from less volatile products; but in that case *i* must be filled with oil or paraffin and heated to 201°.

Girard's apparatus might be improved by bending the connecting-pipe *b* so as to make a hydraulic lute, and thus to prevent the vapours from passing at once to the back part of *k*. Its action would even then be hardly as perfect as that of the more modern column apparatus, which will be described in the 11th Chapter; and it is indeed quite possible (according to private information received from Dr C. Häussermann) to use a Savalle still, such as will be described there, for phenol, with a few slight modifications.

For the distillation of *mother-liquors* and of such fractions as do not separate any crystals on cooling, which, therefore, have been deprived of most of their crystallizable phenol, efficient column apparatus, as shown *supra*, are indispensable. Considering the slight difference in the boiling-points of pure phenol (183° to 184°) and those of the cresols (*o*-cresol 191°, *m*-cresol 203°, and *p*-cresol 204°), this goes without saying. And yet it is possible by means of fractional distillation and partial crystallization, to obtain phenol nearly free from cresols, crystallizing at about 35°, but not entirely, since the resulting mixture of cresols retains from 5 to 15 per cent. of phenol. The result aimed at is: to split up all the mother-liquors, first runnings, intermediate fractions, etc., into crystallizable phenol and a mixture of cresols, boiling upwards of 190°.

The large German tar-distilling works distil the crude phenol in simple stills, provided with a column or with a long head, but for the further splitting-up of the distillates they employ more efficient column-apparatus.

Crystallization of the Distillate.

The above-mentioned principal fraction is left to crystallize in a cool place, in large funnel-shaped vessels with a tap below, through which afterwards the mother-liquor can be drained away. The latter is a solution of phenol in cresol and is redistilled. Its separation from the crystals may be facilitated by a centrifugal machine. A sufficiently low temperature can be obtained during the summer season sometimes by circulation of cold water, sometimes only by a freezing mixture. At larger works a cooling-cellar is employed. It is best not to cool below 12° C., since otherwise the solidifying parts of the product will not come up to the standard.

It is decidedly preferable to charge the crystallizing vessels direct from the cooling room. The first vessels thus yield far more crystals, the cresols accumulating more in the last vessels. These vessels are somewhat deep boxes with handles, made of strong sheet zinc, holding 25 to 40 gall., which can be loosely suspended in a trough filled with running water. When the crystallization is finished, the boxes are placed upside down in a large tray, to draw off the mother-liquor, and the crystals are ultimately further drained in a centrifugal machine with 1500 or 2000 revolutions per minute.

The mother-liquor, and also the third fraction of the first distillate (both separately) are redistilled as described for the first operation, and this is repeated so long as any crystals separate out. It is evident that no general instructions can be given, but that the fractions, which may become very numerous, must be grouped according to their boiling-points, so as to separate the homologues and ultimately cause the boiling-points to become constant within a few degrees, viz., 184° to 188° for carbolic acid and 200° to 203° for cresylic acid. The ordinary crystallized phenol boils at 186°; if the purest phenol, boiling at 182°, is required, the thermometer should be observed accordingly.

For the following detailed description of the manufacture of pure carbolic acid, as practised in Lancashire, I am indebted to Mr Watson Smith:—The crude carbolic acid is distilled in cylindrical wrought-iron stills 2 ft. 9 in. wide, 2 ft. 2½ in. high, with a head 5¾ in. wide, and a thermometer. The worm should be made of zinc—lead, copper, and tin having been tried and failed. Three different fractions are made: first, water, with some oil; second, good, crystallizable oils; third, oils not crystallizing, containing cresols and naphthalene (*cf.* Lowe's prescription, p. 733 *et seq.*). If the crude phenol be good, the second fraction will crystallize on standing. It is well agitated with some highly concentrated and pure sulphuric acid, in the proportion of 1 part acid to 50 parts of phenol by weight; with inferior phenol, 2 parts acid to 50 phenol may be used, but never more: and only one such treatment should be employed; otherwise the oils will not crystallize afterwards. In this process the phenol deepens in colour, turns pink, and becomes perceptibly warm. The mixture, well agitated, is poured *at once* (this is very essential) into the still, and the distillation is commenced and carried through without stopping and starting again. The first products come over between 150° and 160° C.; and the distillate often crystallizes immediately after dropping. Not much comes over below 175°; and it is better to keep this separate. Usually most comes over between 175° and 185°. At this stage the contents of the retort commence to coke, and the process is stopped. The contents of the receiver are allowed to stand for several hours, in order to cool completely and to crystallize. The mass obtained is set to drain for two or three days, the more thoroughly drained upper portions being from time to time removed. To a portion once crystallized no fresh distillate must ever be run, as it would redissolve some of the crystals. Care must be taken not to crush the crystals. The oil that drains from them is technically termed "phenylene." This is again distilled and more crystals obtained from it, which are drained; and the resulting "phenylene" is distilled a third time, but without further treatment with sulphuric acid. In distilling the "phenylene" oils, it is usual to leave in the retort 1½ gall. (sometimes 2) out of every 20, this residue being technically termed "terebene." It is assumed that the latter contains the oils which would prevent the phenol from crystallizing. When the "phenylene" has thus been exhausted by two or three distillations, it is set aside as "bad phenylene."[1]

In lieu of these repeated fractional distillations it has been found advantageous to artificially cool the "phenylene oil" by refrigerating machines.

All the drained crystals obtained as above mentioned are now fused on a water-bath; the liquid is poured into an iron retort with a zinc worm, and distilled—the first small portion

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[1] The terms "phenylene" and "terebene" are used only as private marks, and are not generally employed.—G. L.

(containing water) being rejected, and most of the remainder received into bottles or other vessels, where it solidifies quickly on cooling, forming a white crystalline mass, which is sold as "pure commercial carbolic acid." The small quantity left in the retort is classed as "terebene oil." A purer product than the above is obtained by placing the bottles upside down for a day, re-fusing the drained mass on a water-bath, and pouring it into fresh, perfectly clean and dry bottles or other vessels The liquid now sets perfectly hard and very white, and is termed "finished commercial carbolic acid."

For "finished medical carbolic acid," the first crystals obtained from "phenylene oils" by draining all night are melted into a glass retort, and a little of a mixture of equal parts of sodium bicarbonate and pure litharge or red lead, well mixed and pulverized, is added. A very small quantity of this suffices; the lead oxides probably act by retaining sulphur compounds. After standing for some time, distil into a clean dry vessel, rejecting the portions first coming over, which contain some moisture. The crystals obtained are fused on a water-bath; and the resulting liquid is poured into clean dry bottles, in which, on cooling, it forms pure white and solid crystallized carbolic acid. [The addition of sulphuric acid in the first distillation is not practised anywhere else, and is no doubt the cause of the coking observed at such a low temperature. The dehydration of the phenols is quite easily performed without it. The described process will yield technically pure carbolic acid, but not an article suitable for pharmaceutical purposes. Kraemer (priv. comm.) considers the sulphuric-acid treatment and especially the distillation of the phenol with it, as entirely misplaced, since the distillate will always contain SO_2. He distinctly warns against the method in question.]

The following description of the manufacture of carbolic acid in England comes from an official, and hence authentic, source (*Dr Ballard's Sanitary Report to the Local Government Board*, for 1878, p. 151). Carbolic and cresylic acids are prepared from the crude acids by a series of fractional distillations and crystallizations. For these distillations iron stills, capable of dealing with charges varying from 150 to 500 gall., are used; they are heated by a fire beneath. The crude acid is transferred from the casks in which it arrives at the works to a closed tank, preferably sunk in the ground, from which it is pumped into the still. The residue of the first distillation, which is or ought to be conducted to dryness, is a light and spongy coke, which, when the still is cool, is broken up with an iron bar and removed through the manhole. It is used as fuel. During the last part of this first distillation offensive uncondensable gases are given off. When, on subsequent distillation, an acid is distilled off which solidifies at a higher temperature than that which results from the first distillation, the acid is apt to solidify in the pipe, and hence the pipe leading to the condenser is provided with a short-necked opening, capable of closure, through which, if necessary, hot water may be introduced to clear the pipe. The products of condensation are collected in numerous small fractions, and are usually received in a series of galvanized iron vessels, which are left open during the process of their filtering, but covered with a lid when they have become full. Carbolic acid is most abundant in the earlier, and cresylic acid in the later, fractions. The vessels containing the products of distillation are then set aside to cool, when the carbolic acid crystallizes, while the cresylic acid, holding some carbolic in solution, remains liquid. The liquid matter is then drained off through an opening near the bottom of the vessel, and is subjected to a second distillation for the purpose of obtaining the carbolic acid it contains. When all the liquid has been drained off from the crystals, or removed by the aid of a centrifugal machine, the carbolic acid obtained is again distilled, and the cresylic acid, after crystallization of the carbolic acid in the receiving vessels, is drained off by inverting the latter over a trough. By the first distillation and crystallization, as conducted at Lowe's works, a carbolic acid fusing at 29°·5 C. is obtained. The second distillation and crystallization gives an acid fusing at 35° C. The acids, of the fusing-points mentioned above, are next melted in a steam-jacketed vessel and mixed with water; the liquid hydrate of cresylic acid is separated mechanically in the usual manner; and the solid crystalline hydrate of carbolic acid is submitted to fractional distillation, by which process the fusing-point of the dry acid is raised to 42°·2 C. All these are "commercial" acids, and for medical purposes still require refining, in order to remove from them the last traces of neutral hydrocarbons, of the offensive sulphuretted compounds, tar-bases, etc. At Calvert & Co.'s works the commercial acids are refined by suitable acid treatment for the removal of the bases and neutral hydrocarbons, and by treatment with acetate of lead for the removal of sulphuretted hydrogen. After this the acid is redistilled in glass retorts heated by a sand-bath, each retort taking a charge of about 40 lb., of which four-fifths are distilled off. The residue in the retorts is a blackish, treacly substance which crystallizes imperfectly, and which is dealt with elsewhere for the recovery of such carbolic acid as it contains. The liquid cresylic acid which results from earlier operations is refined in a similar manner by distillation with acetate of lead; but an iron still is used for this process, and the distillation is carried to the production of a coke.

In order to prevent the *nuisance* arising from the escape of offensive uncondensable gases, which are sometimes perceptible for a distance of at least 100 yards, the following arrangement is carried out at Mr Lowe's works. The pipe from the worm condenser, at a distance of a few inches from the place where it issues from the tub, divides into two branches, one of which descends and carries off the condensed liquid, a gas-trap being formed by a bend of the pipe. The other branch ascends and conducts any uncondensed gases to a 6-in. main pipe, which runs along the front of the whole range of stills. From this main a pipe conveys the gases to a small worm condenser, and from this to a stoneware bottle which receives all liquid matters condensed here. A pipe proceeding from this bottle is supplied with a steam-jet, which aspirates the gases from the main and drives them onwards through water or milk of lime, contained in a cask, whereby sulphuretted hydrogen is arrested; and from this washer a pipe conveys the residual gases into the ash-pit of a fire. Should the gases chance to ignite, the ignition would not proceed further back than the cask.

The open receivers, described above, are a source of nuisance, from the general odour of crude carbolic acid. This may be considerably lessened by receiving the condensed liquids into covered vessels, as shown in Figs. 171 and 172. A series of deep narrow pans (*a a*) are set side by side, with intervals of a few inches between them, within a wooden case (*b*), filled with brine, which can thus circulate around and between the pans. All the upper part of the case is closely covered, so that only the tops of the receivers are seen, which are kept covered by wooden covers. The condensed products are conveyed by a pipe (*c*), having small branch pipes with taps opposite the several receiving-pans, which pipes discharge into the pans below their covers. Should any pan become too full, the surplus can be run off from the upper part by a waste-pipe (*d*) screwed into the bottom of the pan, into a drain or channel (*e*) beneath, leading to the liquid acid tank. The brine which circulates round the pans is cooled by means of a freezing-machine. The crystallization of the acid thus takes place more speedily and completely; when it is finished, the pans are uncovered, the pipes *d d* are removed, and the liquid portion then runs off into the drain *e*.

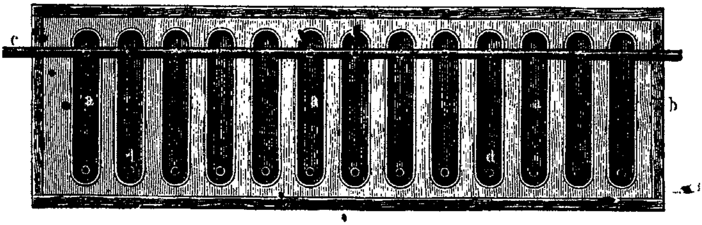

FIG. 171.

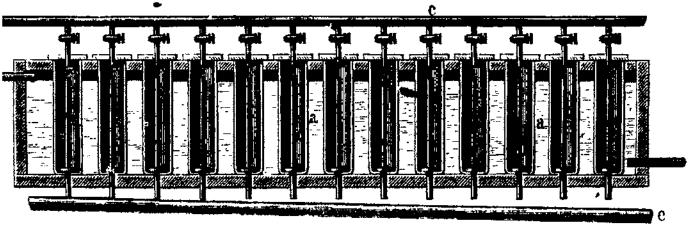

FIG. 172.

[A drawback of the just-described apparatus is this: that the crystallizing-vessels are irremovably fixed in the cooling-tank, which renders it difficult to get the crystals out of these narrow vessels. This might be obviated by *fusing* the crystals, after draining off the mother-liquor, by heating up the cooling-water; but this proceeding would certainly not facilitate the subsequent treatment in a centrifugal machine.

Riehm[1] has described a process for separating phenol and cresols by means of their barium salts, which we shall refer to again when treating of the purification of the cresols.

Absolutely Pure Carbolic Acid.—By the methods hitherto described it is possible to obtain crystallized carbolic acid, but hardly an article remaining white, fusing at 42° and boiling at 182°. On the contrary, the maximum fusing-point thus reached is 38°, and on standing for some time the acid turns red, partly liquefying, the liquid portion being discoloured. The lower melting-point is not caused by the presence of water, but by para- and orthocresols, which cannot be removed by fractionation, as the boiling-points differ too little (phenol 182°, orthocresol 185° or 186°). But a separation can be founded on the fact that carbolic acid forms with water a crystallizable *hydrate*, whilst the cresols yield liquid hydrates.

This observation was first made in 1862 by Lowe, who thereupon founded the manufacture of purest carbolic acid.[2] He added to fused crystallized carbolic acid a certain quantity of water, and cooled down to 4° C.; thus he obtained a phenol hydrate, $C_6H_6O+H_2O$, crystallizing in large octahedra, from which the mother-liquor, containing all the cresols, could be separated by draining and centrifugalling. The hydrate on distillation yields first water and then phenol, fusing at 41° and boiling at 182°.

Some more details are given in Lowe and Gill's patent.[3] To ordinary phenol, according to whether it crystallizes at 16°·5 or 35° C., from 5 to 30 per cent. water is added, with heating and agitating, the solution being afterwards cooled down to $-9°{\cdot}5$ or $+10°$, and the crystals treated as above. The product may be obtained absolutely pure by repeating his treatment.

Crace Calvert (*loc. cit.*) believed the composition of the hydrate to be $(C_6H_6O)_2,H_2O$, but Alexejew[4] could not obtain such a hydrate.

Church[5] purifies phenol by precipitating it from its aqueous solution by common salt and distilling over quicklime. This is impracticable, on account of the great loss of carbolic acid.

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[1] Ger. P. 53307.

[2] Crace Calvert, *Chem. News*, 1867, pp. 57, 297, 310, 320.

[3] *Cf.* Marzell, *Chem. News*, xxxvii., p. 105.

[4] *Chem. Centr.*, 1881, p. 51.

[5] *Chem. News*, xxiv., p. 173.

The process now generally employed for the preparation of absolutely pure phenol is substantially that of Lowe and Gill, and is carried out on the large scale as follows:—Crystallized carbolic acid, purified by distillation in the ordinary manner, is once more distilled, by an open fire or preferably by high-pressure steam, with the aid of a vacuum, in a wrought-iron still holding from 1 to 5 tons, and working very slowly. The first runnings contain a little water; the principal fraction is carbolic acid, fusing at about 35°, and the distillate is turned into another receiver when the fusing-point falls below 25°. This last product is combined with the corresponding portions of the first distillations. The principal, purer fraction is fused in enamelled iron pans in the water-bath, stirred with 5 or 10 per cent. distilled water, and allowed to cool. The phenol hydrate separating out is drained, centrifugalled, and again distilled. For this purpose the still must be provided with an enamelled or (preferably) silver head. The cooling-worm must not be made of iron; if the still-head is long enough, the worm may be made of stoneware, but the connection between them must be below the level of the cooling-water, to prevent cracking of the stoneware. Since the price of silver has gone down very much, it is also used for the worms. Iron enamelled inside has not turned out practicable; aluminium (recommended by Donath, *Z. angew. Chem.*, 1895, p. 141) is entirely excluded, since Zmerzlikar (*ibid.*, 1895, p. 468) noticed that it is strongly attacked by carbolic acid.

The first distillate consists of an aqueous 5 per cent. solution of carbolic acid (saleable as such) and a lower layer of pure carbolic acid, liquid on account of containing some water, which is put back into the still for the next operation. The second fraction is pure carbolic acid, fusing at 41° or 42°, which is at once put into the (properly cleaned) tins or glass bottles in which it is to be sent out for sale. The small residue in the still is worked up again in the first distillation.

In many factories the hydration of the phenol, for the purpose of purifying it, is not any more carried out. Phenol sufficiently pure for all technical purposes is obtained by a simple distillation in column-apparatus, which nowadays are supplied in such a state of perfection that the distillate does not require the troublesome process of purification by means of the hydrate. Of course the crude oil, the alkaline extract, and the crude carbolic acid must be previously subjected to the purifying processes described *supra.*

The separation of phenol from the cresols is effected in quite a different way by the process by A. Friedlænder (Ger. P. 181288), founded on the observation, made by him, that phenol is soluble in *dilute* solutions of the sulphonic acids of aromatic hydrocarbons, or the salts of the same (*e.g.*, potassium or sodium benzol-sulphonate or toluol-sulphonate), whilst the cresols are only soluble in *concentrated* solutions of these compounds. This process is carried out by mixing the tar-oil at the ordinary temperature with a concentrated aqueous solution of one of the above-named salts, just sufficient for dissolving the phenols, as empirically ascertained according to their total contents of phenols, in an apparatus provided with a mechanical agitator or with agitation by compressed air, and separating the two liquid layers formed. After steaming the aqueous solution up to clearness, as above described, it is diluted with ten times its volume of water, whereby the cresols are completely excreted and can be separated from the solution of phenol in the dilute solution of sulphonate. By treating this with benzol, the phenol is completely extracted from that solution which, after concentration, goes back into the process. From the solution of phenol in benzol the solvent is driven out by means of steam, and the pure phenol recovered in an anhydrous state.

Synthetical Production of Carbolic Acid.

Carbolic acid in the pure state is also produced synthetically from benzene, by the reaction of Wurtz, Kekulé, and Dusart:

$$C_6H_6 + SO_4H_2 = H_2O + C_6H_5(SO_3H).$$

Benzol is by means of fuming sulphuric acid converted into benzol-monosulphonic acid. The product of the reaction is neutralized by milk of lime; the solution of calcium benzol-sulphonate is separated from the solid calcium sulphate; the solution is decomposed by sodium carbonate, and the filtered solution of sodium benzol-sulphonate evaporated to dryness.

From this salt, by fusion with caustic soda, sodium phenolate is obtained:

$$C_6H_5.SO_3Na + 2NaOH = C_6H_5ONa + Na_2SO_3 + H_2O,$$

and is worked up in the well-known manner.

The yield obtained by this process is very good. Usually 200 kg. sodium benzol-sulphonate is fused in a cast-iron pot with 100 kg. sodium hydrate. The separation of phenol from the solution of the fused mass by means of carbon dioxide is rather complicated by the presence of the sodium sulphite, since the process would not pay when losing the sulphite.

This process is described in detail by Ney (*Chem. Trade Journ.*, 1915, lvii., p. 361). It formerly could not be considered as commercially practicable, but the British Consul at Stuttgart reports officially in 1902 that the prohibition of the exportation of carbolic acid from Great Britain in January 1900 had caused the German manufacturers to produce carbolic acid by synthesis (*Chem. Zeit.*, 1903, p. 229).

At the present low price of carbolic acid, and owing to the very high demands on the purity of the phenol of trade, the synthetical production of that compound has receded into the background.

The synthetical phenol, like the phenol obtained from coal-tar, turns red by the action of light (as found by Schneider, *Chem. Ind.*, 1892, p. 118), but the former, unlike the latter, is nearly devoid of smell. It is strange that just that property interferes with its sale for pharmaceutical purposes, since the pharmacists consider the smell of carbolic acid as an essential property of it.

The Chemische Werke Ichendorf at Horrem, near Cologne (Ger. P. 281175), produce monovalent phenols synthetically by heating mono- or dichlor-substitution products of aromatic hydrocarbons with the hydroxides of alkaline metals and methyl-alcohol.

Böhringer (Ger. Ps. 286266 and 288116) also produces phenols from mono-substituted aromatic hydrocarbons.

The Reddening of Carbolic Acid.

Phenol, even that which has been obtained synthetically from benzol, has the property of turning red under the influence of light and other agencies. This circumstance causes a good deal of trouble to the manufacturer, since he is called upon in many cases to supply phenol which is not merely colourless, but remains so for a long time on being kept. This phenomenon occurs with many products of coal-tar, but in no case as strongly as in that of phenol, and it has been the subject of a great many investigations, which, unfortunately, have given partially contradictory results, and we can mention them only briefly in this place.

It is certain that the reddening of phenol only takes place under the influence of *light*, but equally certain that other agencies are required as well; on this point the opinions and the results of the different authors vary very considerably.

Ammonia, in the shape of traces of ammonium nitrite, getting into the transportation vessels from the air during the filling, is accused by Hager (*Pharm. Zentr.*, 1880, p. 77; 1883, p. 447) as causing the reddening of phenol. Mylius (*ibid.*, 1887, p. 72) is of the same opinion, as he found that an addition of hydrochloric acid up to a distinct reddening of litmus-paper prevented the reddening of carbolic acid, even in glass bottles; but this does not help in all cases.

Several authors believe that traces of *metals* or *metallic compounds* cause the reddening. Sicha (*Chem. Zentr.*, 1892, p. 486) mentions copper; Meyke (*Pharm. Zeit. f. Russland*, 1893, xxii., p. 427) lead; Fahlbusch (*Pharm. Zentr.*, 1885, p. 6) iron. According to experiments made by Kreusel (*Chem. Ind.*, 1886, p. 84) the reddening is principally caused by copper, whilst silver, lead, or zinc have less action in this way, and tin none at all. He isolated the colouring substance which is soluble in sulphuric acid with blue colour, and therefore cannot be rosolic acid, as formerly assumed, since this dissolves in sulphuric acid with yellow colour.

Most authors ascribe the reddening of carbolic acid to *oxidation* processes, which are assumed to take place in various ways. In the first line *rosolic acid* is thought of, *e.g.*, by Yoon (*Pharm. J.*, 1882, p. 1051). Hanks (*Math. naturw. Ber. aus Ungarn.*, 1892; *Chem. Zeit.*, 1895, p. 1143) also finds that the reddening of carbolic acid is caused by oxidation, which is promoted by the presence of metals (especially copper), and of ammonium compounds. Tin protochloride prevents the reddening, probably owing to its reducing action. The colouring matter is less volatile than carbolic acid, and therefore remains behind on distillation. Its behaviour proves that it is not coralline, as assumed by some authors. It reddens carbolic acid distinctly when diluted 1 : 200,000. According to this author, the reddening of carbolic acid can be prevented by putting into the stock bottles a few crystals of stannous chloride before filling them with carbolic acid, and shutting them up tightly. Also keeping the phenol in well-tinned metallic vessels does good service.

P. W. Hofmann has taken several patents for employing protochloride of tin to prevent the reddening of carbolic acid, which he ascribes to the precipitation of the impurities (Ger. Ps. 65131, 67693, 67696, all in 1892).

J. Walter (*Pharm. J.*, 1898, p. 706) seeks the cause of the reddening of phenol in the presence of *iron compounds* in the glass bottles, which in the presence of air and moisture causes the formation of hydrogen peroxide. By producing a thin coating of paraffin on the inside of the vessels, the phenol can be kept permanently colourless, as he asserts.

Kraemer believed the reddening to be caused by the presence of certain *aldehydes* (*J. Gasbeleucht.*, 1887, p. 849). According to a later communication made by him to the author of this book, the reddening is caused by a little *benzoic acid*, contained in crude phenol, and passing over when distilling it; it takes up some iron from the still and forms ferrous benzoate, which by the action of atmospheric oxygen is changed into red ferric benzoate. He, as well as Spilker (*Berl. Ber.*, 1896, p. 3) mentions *indene* as belonging to the class of colouring compounds. Bidet (*Monit. Scient.*, 1889, p. 487) states that *thiophene* causes the coloration of carbolic acid, as well as that of aniline and toluidine, but only in the presence of light, whereby oxidation is caused.

H. D. Gibbs (*Chem. News*, 1909, c., pp. 68, 81, 94) has made an extensive investigation on the reddening of phenol, with the following results:—Pure phenol remains colourless in sunlight. In contact with indifferent gases (hydrogen, nitrogen, carbon dioxide) and oxygen, it is not sensibly coloured in the dark at ordinary temperatures, but distinctly so at 100°, and pretty rapidly at the boiling-point of phenol, owing to an oxidation, whereby quinol, quinone, catechole, and a little carbon dioxide are formed. The coloured products are principally condensation products of quinone, especially phenoquinone. Active oxygen, in the shape of ozone and of anodic oxygen, quickly and easily combines with phenol, but the experimental results speak against the action of gaseous oxygen ions. The glass of the bottles has influence on the speed of the reaction; this is diminished by glass possessing a strongly absorbing action in the ultra-violet rays. The speed of the reaction is also influenced by the height of the sun over the horizon, by the density of the atmosphere, and by the atmospheric conditions. Ozone could not be detected in pure, molecular oxygen, exposed to sunlight. Anisol is not coloured in the sunlight by ozone or oxygen. The purest phenol cannot be distilled without change, except in the absence of oxygen, preferably in a hydrogen atmosphere.

Fabini (*Chem. Ind.*, 1892, p. 148) found that the colouring substance can be prepared in considerable quantities by the action of cupric sulphate upon ammonium phenylate. It is a black, resinoid substance, which he calls "phenythren," which on heating forms a yellow vapour and sublimes in the shape of a pink body soluble in concentrated sulphuric acid with blue colour. It leaves no ashes and therefore contains no metal; the metals active in its formation play only an intermediate part by forming metallic phenylates, decomposed by hydrogen peroxide into colouring-matter and metal. 0·004 g. suffices for imparting a slight pink shade to 1 kg. of carbolic acid; 0·1 g. gives a dark red colour.

Kohn and Fryer (*J. Soc. Chem. Ind.*, 1893, p. 197) in an extensive investigation found that the chemically pure ("absolute") phenol of commerce, specially purified by 15 redistillations, showed the same reactions as synthetic phenol and that made from the salicylic acid of winter-green oil. All of these phenols were coloured by pure hydrogen peroxide without the presence of metallic compounds, but the latter hastened the reaction. Concentrated ammonia imparts to phenol a blue colour; dilute ammonia, caustic potash, hydrogen peroxide, a pink colour; light has only a quickening action. Thoroughly dry air does not act upon phenol, nor does water in the absence of air; but moisture in the presence of air reddens phenol even in the dark, and more quickly in the light.

Richardson (*ibid.*, 1893, p. 415) on repeating Kohn and

Fryer's experiments, found that under all circumstances hydrogen peroxide is formed when phenol meets with moist air, and that this is the reddening agent. Like Kohn, he found that behind dark red glass no reddening took place, but no H_2O_2 was formed in this case.

Boes (*Pharm. Zeit.*, 1902, p. 448) explained the reddening by the presence of the "isophenols," indicated by Brunner, but this will hardly hold good, since Brunner himself later on found that his "isophenols" did not exist (*Chem. Zeit.*, 1902, p. 1123).

According to Ebell (*Rep. f. anal. Chem.*, 1884, p. 17) crystallized crude carbolic acid contains substances which are volatile and colourless, but are changed into non-volatile, red, or yellowish-brown substances by the action of light more than by that of heat and air. The substance yielding the red colour passes over principally along with the first, that yielding the yellow colour with the last products of distillation. Neither of them in partial crystallization enters into the crystals of carbolic acid, apart from what is mechanically enclosed in them, but remains in the mother-liquid. They are sparingly soluble in water, but are extracted by water acidulated with sulphuric or phosphoric acid; they are insoluble in benzene. Oxidizing agents, acting during the distillation, change the substance yielding the red colour more than that yielding the yellow colour; oxidizing agents in aqueous solution and in the presence of sulphuric acid destroy them both. The products of oxidation seem to be less soluble in water than the original substances; they are not volatile, or pass over only with the highest-boiling fractions. Even the carbolic acids distilled from glass vessels often colour very strongly; in such acids no traces of metals could be found.—It is recommended to purify the crude acid by repeated crystallization and subsequent distillation of the crystals. If it is not possible to work up the red mother-liquors, or to sell them at a fair price as "100 per cent. liquid carbolic acid," it is recommended to treat them with an oxidizing agent in the presence of sulphuric acid, and to follow this up by repeated washings. In less difficult cases it is sufficient to add to the contents of the retort, previous to distillation, a little red oxide of lead with a small admixture of sodium bicarbonate, or some finely pulverized barium peroxide.

Processes for preventing the Reddening of Carbolic Acid.

In the preceding account of the various explanations of this phenomenon we have already mentioned some of the proposals made for preventing it.

We will now enumerate some further proposals for the object in question, although all of them appear superfluous, if the carbolic acid is properly fractionated and the solution of sodium phenolate is carefully purified.

We first mention the process of H. Müller (*Dingl. polyt. J.*, clxxix., p. 461), who at the same time introduces fractional precipitation (analogous to the fractional saturation mentioned by Behrens, p. 733) of the crude carbolic acid before distillation. The alkaline carbolic liquid contains, besides carbolic acid, some oxidizable bodies which give rise to a brown coloration, and also, especially in concentrated solutions, a considerable quantity of naphthalene and other indifferent substances insoluble in water by themselves. It is diluted with water till further addition ceases to precipitate naphthalene;[1] the dark brown liquid is exposed to the air in a shallow vessel for several days, with frequent stirring; it is then filtered, its percentage of phenols ascertained, and the quantity of sulphuric acid necessary for precipitating the whole of them calculated. If now only $\frac{1}{8}$ or $\frac{1}{8}$ of the calculated acid is added with frequent stirring, at first the resinous substance, changed by the action of the air, is precipitated, mixed with more or less of the phenols. A further addition of acid precipitates essentially cresol; and after a few trials almost pure phenol, crystallizing after a single distillation, can be obtained by the third and last precipitation. In order to remove the water, a current of dry air is passed over the phenol heated almost to boiling. The aqueous vapour is usually accompanied by an unpleasantly smelling substance, according to Müller a sulpho-compound of phenol, which can be removed by adding a little lead oxide before distilling. (Such sulphur compounds no doubt exist already in the tar; but they may also be formed afterwards by incautious precipitation with strong sulphuric acid, as pointed out, p. 744.)

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[1] This stage of the dilution is not very easily ascertained; hence it is preferable to employ dilute alkali from the first, as already pointed out.

The exposure of the liquor in shallow pans with frequent stirring, recommended by Müller, would no doubt be advantageously replaced by forcing in a finely divided current of air, or by running the liquor down a coke column, etc. The same object is attained, according to Stohmann-Kerl's *Chemie*, vi., p. 1182, by adding $\frac{1}{4}$ or $\frac{1}{3}$ per cent. potassium bichromate, and the sulphuric acid necessary for decomposing this, to the crude carbolic acid in the still, and heating gently at first. If this does not suffice to make the phenols distil colourless, more bichromate must be added.

It has been recommended (*Chem. Zeit.*, 1884, p. 1338) to treat crude (50 per cent.) carbolic acid with 1 per cent. of potassium bichromate and the corresponding quantity of strong sulphuric acid in a shallow pan, running in first the acid, then the solution of bichromate, and agitating the mixture for several hours with access of air and in a place exposed to the direct light of the sun. The mixture is allowed to settle, the oil is drawn off and distilled, and the fraction coming over between 170° to 198° is again submitted to the bichromate treatment, and is redistilled in a still with rectifying-column.

Reuter (*Chem. Zentr.*, 1905, i., p. 1012) contends that the reddening of phenols can be prevented by the use of a small quantity of sulphurous acid, and redistilling in a current of CO_2, to exclude air. He recommends that the pharmacopœias should directly prescribe the colour of carbolic acid to be red!

Demant (*Chem. Zeit.*, 1887, p. 78) liquefies red carbolic acid in a water-bath, with addition of 10 per cent. spirit of wine, and cools down. When most of the liquid has solidified, the mother-liquor is drained off; the crystals are then again obtained in a white state.

From the above we may conclude that, in the manufacture of carbolic acid, it is no use trying to prevent the reddening under any circumstances. Good drying and keeping away metallic contaminations will delay, but not entirely prevent, the reddening, nor will this be done by the addition of oxidizing agents in the distillation; since the purest phenol reddens in the presence of air and moisture. But it is certain that the red colouring-matter is entirely harmless for medicinal uses.

Marzell (*Chem. News*, xxxvii., p. 105) recommends an addition of alkaline plumbate solution for decomposing the *nauseous sulphur compounds.* This is probably better than Müller's plumbic oxide (*supra*, p. 770), or than the addition of red lead and sodium bicarbonate, as practised in Lancashire according to Watson Smith (p. 758). Casthelaz employs a solution of sodium bisulphite for a similar purpose.

Sharpe's paper on the manufacture, purification, and application of carbolic acid (*J. Soc. Dyers and Col.*, 1884, p. 146) can only be mentioned here.

Commercial Cresols.

A large quantity of products, consisting essentially of a mixture of the three isomeric cresols with a little phenol and xylenols, is produced especially by the German tar-works, as a by-product from the manufacture of pure carbolic acid, obtained by fractionation of the crude carbolic acid.

These products are sold by the name of *Rohkresol* (crude cresol), "crude carbolic acid 50 per cent." and "crude carbolic acid 25 per cent." A special investigation of these products has been made at the German Board of Health, by Carl Fischer and P. Koske, and is published in the *Arb. d. Kais. Ges. Amts.*, xix., p. 577-671, abridged in *Chem. Zentr.*, 1903, i., 384-5. We shall quote the most salient points of that work.

Rohkresol consisted of:—

0·35	per cent.	water.		
2·34	„	phenols, boiling up to 188° (a mixture of phenol and cresols).		
94·5	„	mixture of the three isomeric cresols, boiling	from	188° to 202°.
1·23	„	mixture of cresols with a little xylenols,	„	202° „ 210°.
0·06	„	higher phenols „ „	„	210° „ 225°.
0·07	„	residue.		

Traces of pyridine bases

"Crude carbolic acid 50 per cent." showed in 100 phenols · 27·6 per cent. cresols, 54·10 per cent. mixture of cresols and xylenols, 10·90 per cent. highest boiling phenols; first runnings, etc., 7·40 per cent.

"Crude carbolic acid 25 per cent." showed in 100 phenols: 4·02 first runnings, 22·66 cresols, 43·60 mixture of cresols and xylenols, 6·90 xylenols, 3·94 phenols boiling from 220° to 270°, 15·98 phenols boiling over 270°. Besides the phenols (25 per cent.), there were 75 per cent. non-phenolic substances." The authors tested these products, as well as a number of other commercial carbolic-acid preparations, for their bacteriological action, but into this we cannot enter here.

Liquid Carbolic Acid, water-white, consists of the redistilled mother-liquors from crystallized carbolic acid containing the three cresols (sold by the firm of Schering as "*tricresol*"). Hammerl (*Z. angew. Chem.*, 1897, p. 569) states that its bactericidal properties are twice as strong as those of a solution of carbolic acid of equal percentage. The fault of slight solubility has been remedied by the preparation of "*lysol*" and "*creoline*" (pp. 660 and 658).

The mother-liquor remaining after completely exhausting all the crystallizable carbolic acid contains but little carbolic acid, together with all the cresols. It forms a limpid liquid boiling at 182° to 200°, and has a disagreeable smell, quite different from carbolic acid. The boiling-points of the isomers do not differ very much:—

Orthocresol	191°.
Metacresol	203°.
Paracresol	202°.

Hence their separation by fractionation is not possible, all the less as their relative proportions are not always the same. Both Ihle (*J. prakt. Chem.* [2], xiv., p. 451) and Tiemann and Schotten (*Berl. Ber.*, xi., p. 168) found mostly ortho- and paracresol, with little metacresol; but K. E. Schulze (*ibid.*, xx., p. 410) found about 40 per cent. meta-, 35 per cent. ortho-, and 25 per cent. paracresol in tar-oils. Weger (*Z. angew. Chem.*, 1909, pp. 391 *et seq.*) states that the percentages of the three isomeric cresols differ very much in different commercial cresols.

Gruber (*Fischer's Jahresber.*, 1893, p. 539) found that water of ordinary temperature dissolves 2·5 per cent. (by volume) of pure ortho-, 0·53 per cent. of pure meta-, 1·80 per cent. of pure paracresol, 2·20 per cent. of the mixture of cresols prepared from toluidine, 2·55 per cent. of that prepared from tar-oil.

Nördlinger (*Z. angew. Chem.*, 1894, p. 166) states the following properties of tar-coal cresol:—Water dissolves 2 to 3 per cent., and is itself soluble in cresol in the proportion of 15 or 20 to 100 cresol. Cresols are easily soluble in animal, vegetable, and tar-oils, less so in "mineral oils." They dissolve

20 to 30 per cent. of mineral oils. The reciprocal solubility of cresol and oils increases with the percentage of oils, and decreases with that of water. Anhydrous concentrated oily solutions of cresol attract water, and are ultimately separated into two layers, one of aqueous cresol and the other of oil floating above. Much water is able to extract cresol from its solution in oil, but by shaking with oil cresol can also be extracted from aqueous solutions.

The *poisonous and antiseptic properties* of the three cresols, according to Gibbs and Hare (*Arch. d. Physiol.*, 1889, p. 289) are different. The lethal doses for 1 g. of nervous substance of the frog are 0·004 ortho-, 0·006 para-, and 0·044 metacresol. Quite a number of communications have been made on this point in 1906 and 1907, and are reported upon in *Chem. Zentr.*, 1906, ii., pp. 1510, 2070; 1907, i., p. 835; ii., pp. 85, 2070.

J. Herzog (*Apoth. Zeit.*, 1907, p. 78; *Chem. Zeit. Rep.*, 1907, p. 73) makes the following statements: *o*-cresol (b.-p. 190°·8) has least action; *p*-cresol (201°·8) is most poisonous; *m*-cresol (202°·8) is the most efficient antiseptic.

Rapp (*Chem. Zentr.*, 1907, ii., p. 717), on the contrary, finds that *o*-cresol is at least equal in bactericidal action to *p*-cresol, and almost as much so as *m*-cresol. According to the same author (*ibid.*, 1909, ii., p. 2206) the disinfecting power of *m*-cresol is the strongest; then follows *o*-cresol, and at last *p*-cresol. This power is lessened by contamination with light hydrocarbons, pyridine, and anthracene, but increased by "neutral oil"; naphthalene does not appear to have any influence in that respect. The cresols obtained from creosote oil, *e.g.* creolin (*vide supra*, p. 773), are more efficient disinfectants than those obtained from carbolic oil. The separation of the *o*-cresol in the preparation of cresolic soaps does not yield any more strongly disinfecting products; therefore the cresolic soap, prepared according to the Prussian ministerial publication of 19th October 1909, is not an equally good disinfectant as the original lysol. The crude cresols of trade exhibit quite different disinfecting powers; those containing much *o*-cresol seem to be the best, but these also, when dissolved in potash-soaps, do not come up to lysol.

The medical cresol should be a yellow or brownish liquid of neutral reaction, easily soluble in alcohol and ether, clearly soluble in 100 parts of cold water, boiling at 198° to 202° C. With this crude cresol and a linseed-oil soap (containing 70 per cent. fatty acid) a solution of cresolic soap is obtained, equal in disinfecting power to lysol.

These properties are important in connection with the application of the cresols for disinfecting purposes, for which, according to several authors, the tar cresols are much more efficient than pure carbolic acid; in solutions of the same percentage, Hammerl (*Arch. Hyg.*, xii., p. 359) found the former from four to ten times as efficient as the latter, and similar results have been published by Deplanque (*Bull. thér. Arch. Pharm.*, 1888, p. 453), Gruber (*Jahresb. Fortsch. Pharm.*, 1893, p. 389), and Seybold (*Chem. Zeit.*, 1899, p. 35).

Utz (*Chem. Zentr.*, 1906, ii., p. 1286) finds the refractive index of the crude cresol (mixture of all three isomers) = 1·5414 to 1·5444; that of the three isomers: $o = 1{\cdot}5492$, $m = 1{\cdot}5402$, $p = 1{\cdot}5416$, all at 15° C. Genuine lysol (p. 660) = 1·5068.

Separation of the Three Isomeric Cresols.

Quite a number of processes has been worked out for this object, since the pure isomers of cresol are required for preparing colouring matters, etc.

Riehm (Ger. P. 53307, 1889) utilizes the various solubilities of barium phenolate and cresylates in water. The mixture of phenol and cresols, previously purified by fractional distillation as much as possible, is treated at an elevated temperature with as much water and barium hydrate as is required for neutralizing and dissolving the phenols. This solution is purified by decantation or filtration from the insoluble matters, and blowing out by steam. The solubility of the various barium salts in boiling water is as follows: barium phenolate requires 40 per cent., barium orthocresylate 150 per cent., and barium paracresylate 350 per cent. of its weight of water at 100°. During the evaporation of the solution the barium salts of phenol, ortho- and paracresol are separated in the form of crystals, whilst the metacresylate remains in the mother-liquor and can be recovered from this as a non-crystallizable, greasy mass. The crystallized salts are freed from adhering mother-liquor by pressing or centrifugalling, and recrystallized as follows:—A quantity of water is added to them, equal to half the weight of the *phenol* (C_6H_5OH) supposed to be present, the mixture is heated to boiling and filtered hot; this solution contains mainly barium phenolate. The residue remaining on the filter is mixed with 1½ times the quantity of *orthocresol* assumed to be present, whereby this isomer is dissolved. The crystalline mass now remaining is treated with 3½ times its weight of *paracresol*-barium, which is prepared from the solution. The single fractions are purified by recrystallizing, and ultimately the pure phenols precipitated by hydrochloric acid. Another form of this process consists in successively precipitating the phenols by addition of hot baryta solution.

Lederer (Ger. P. 79514, *Z. angew. Chem.*, 1895, p. 114) bases his process on the various solubilities of creosoxacetic acids in benzene and the sodium creosoxacetates in water.

The Chemische Werke vorm. Byk (Ger. P. 109418) effect the separation by means of molecular compounds of the cresols with calcium chloride, and many other inorganic and organic salts ("crystal-phenols"). This patent lapsed already in 1901.

Rud. Rütgers (Ger. P. 137584; B. P. 286, of 1902) introduces anhydrous oxalic acid into the crude mixture of cresols, previously freed from phenols while heating the mixture. Thus the oxalic ester of paracresol is formed, which separates out on cooling and is decomposed by water. Ortho- and metacresol are afterwards separated by fractionating. This patent, as well as an additional one (Ger. P. 141421), in which, in lieu of oxalic acid, oxalates were recommended, lapsed in 1905.

Vidal (Fr. P. 315605, of 1901) treats the crude cresols with the sulphate of zinc, calcium, or aluminium, and a nitrate, whereby an insoluble metallic nitroso-derivate of paracresol is formed.

The Chem. Fabr. Ladenburg (Ger. P. 148703; B. P. of Schulze and Ladenburg, 1881, 1904) separate *m*- and *p*-cresol by sulphonating them at a temperature of 110° C. with sodium bisulphate containing sodium pyrosulphate. This transforms *m*-cresol into its sodium sulphonate, while the *p*-cresol is not acted upon. The same inventors (Ger. P. 152652) also prepare a crude (71 per cent.) *m*-cresol from the mixture of calcium cresolates, formed by milk-of-lime; the neutral calcium *m*-cresolate, being very little soluble, is precipitated and is separated from the solution containing most of the *p*-cresol (*Chem. Zentr.*, 1904, ii., p. 108).

The Farbenfabriken vorm. Bayer & Co. (B. P. 9953, of 1904), in order to separate mixtures of *o*- and *p*-cresol, add to these a suitable quantity of KOH, and heat the mixture till solution has taken place. The crystals of the *p*-compound, which deposit on cooling, are separated by filtration, washed with alcohol and treated with hydrochloric acid to separate the *p*-cresol. The filtrate from those crystals is also treated with hydrochloric acid to obtain *o*-cresol.

Raschig (Ger. P. 112545), after having removed most of the *o*-cresol by fractional distillation, separates *p*- and *m*-cresol by sulphonating the mixture. On diluting and cooling, the *p*-cresol-sulphonic acid crystallizes out as such, or in the shape of its sodium salt. The sulphonic acids are decomposed by superheated steam, and yield the pure cresols. Or else (Ger. P. 114975) the sulphonated mixture is at once treated by superheated steam at a certain temperature, whereby only metacresol is split off and distils over, after which the paracresol-sulphonic acid is split up in the same manner at a higher temperature.

Raschig (*Z. angew. Chem.*, 1900, p. 759) has also worked out another process for separating *m*-cresol from *p*-cresol (Ger. Ps. 144903 and 146752). Commercial cresol on an average contains 40 per cent. *o*-cresol, 35 *m*-cresol, and 25 *p*-cresol. When treated with nitric acid, the *o*- and *p*-cresol are destroyed, and 60 parts of pure trinitro-*p*-cresol are obtained. To avoid the great loss of nitric acid in this operation, at least partially, it is expedient to separate by a number of careful fractional distillations the *o*-cresol, boiling at 188° C. Since both *m*-cresol and *p*-cresol have the same boiling-point, 199°·5 to 200°, they cannot be separated by fractionation, but the mixture of 60 per cent. *m*-cresol and 40 per cent. *p*-cresol presents already a great advantage over the first material, as it yields 100 parts of trinitro-*m*-cresol, and wastes less nitric acid. That mixture now forms an article of trade and in it the percentage of *m*-cresol can be estimated by a process which will be described later on. According to a communication made in the year 1909 by Dr Raschig to the author of this book, his factory at that time was the only one which separated the isomeric tar cresols on a manufacturing scale, and sent them out into trade in the pure state. The quantity produced at that time was about 100 tons orthocresol, 100 tons metacresol, and 50 tons paracresol per annum, but he expected it to increase largely.

Terrisse (Ger. P. 281054) separates the three cresols by treating the mixture of cresols with sulphuric acid of about 60° Baumé at diminished air-pressure, neutralizing the so obtained mixture of sulphonic compounds with sodium carbonate, driving off the *p*-cresol by means of steam, decomposing the sodium sulphonates, remaining behind, by sulphuric acid, and ultimately decomposing the *m*-cresol-sulphonic acid by distillation with superheated steam.

F. Hoffmann-Laroche & Co. (Fr. P. 454534; Ger. Ps. appl. H53079 and 54060, of 1911) also separate *m*- and *p*-cresol, and prepare pure *m*-cresol from the commercial mixture by means of converting them into sulphonic acids; the difference against previous processes (Raschig, Chemische Fabrik Ladenburg) consists in the application of a lower sulphonation temperature (so that there is next to no need for heating from without), in using much smaller quantities of sulphuric acid, and in separating solid *m*-cresol-sulphonic acid in such a form that it can be at once employed for preparing other derivatives of *m*-cresol. Two examples are given. 1. Treat 1000 kg. of a mixture of about 60 per cent. *m*-cresol and 40 *p*-cresol with 750 kg. Nordhausen sulphuric acid (containing 20 per cent. SO_3) at a temperature below 100°, with good agitation. Mix the product obtained with 500 kg. sulphuric acid (50 per cent. H_2SO_4), and extract the non-sulphonated cresol by means of benzol at about 50°. On slowly cooling, *m*-cresol-sulphonic acid crystallizes out (with a little *p*-acid), and can be split up into *m*-cresol and sulphuric acid by treating it with superheated aqueous vapour. The benzolic extract, after distilling off the solvent, yields *p*-cresol, which solidifies on cooling. 2. Dissolve 1000 kg. of the mixture of cresols in 500 kg. benzol, and add 950 kg. sulphuric acid of 96 per cent., at 40°, well agitating. After the sulphonation has been effected, dilute with water or dilute sulphuric acid, draw off the benzol which keeps part of the *p*-cresol in solution, and allow the acid liquor to cool. Here also *m*-cresol-sulphonic acid crystallizes out, but not free from *p*-cresol-sulphonic acid; the mother-liquor on splitting up yields a mixture containing more *p*-cresol than the original substance.

Pure m-cresol is obtained from the *m*-cresol obtained by either of these processes by repeating the treatment. In the same way pure *p*-cresol can be obtained from the ordinary commercial *p*-cresol.

Yield of Pure Products from Crude Carbolic Acid.

In Muspratt-Stohmann's *Chemie*, 3rd ed., vol. vi., 1884, this is stated as follows:—

Sources of the tar.	Nature of the starting material subjected to the alkaline treatment.	Pure product boiling between 188° and 203°.	Crystallized carbolic acid obtained therefrom.	Liquid carbolic and cresylic acids.
		Per cent.	Per cent.	Per cent.
South Germany	Light oil.	34·7	13·1	21·6
Do.	Creosote oil.	44·8	...	44·8
Saxony	Light oil.	33·1	13·9	19·2
Saxony, Rhineland, Vienna	?	30·4	6·0	24·4
Sundry	Light oil.	43·7	29·8	13·9
South Germany and Saxony	Light oil.	41·0	28·0	13·0

The considerable loss which takes place in the working-up of crude carbolic acid is caused by its percentage of empyreumatic products, neutral hydrocarbons (especially naphthalene), tar-acids boiling above 203°, and working-losses.

According to Wurtz (*Dictionnaire de Chimie*, ii., p. 820) sundry tars contain the following quantities of "phenol" [which probably means all "tar-acids"]:—

Tar from Wigan cannel coal	14 per cent.
" Staffordshire coal	9 "
" Newcastle coal	5 "
" Boghead	5 "
" certain kinds of peat	15 to 20 per cent.

Watson Smith gives the following analysis (by Lowe's method, see p. 787) of crude carbolic acid from Manchester and Blackburn tar, both made from Wigan cannel coal:—

	Blackburn.	Manchester.	Manchester.
	Per cent.	Per cent.	Per cent.
Water (per cent. by volume)	12	13	15
First oil, boiling up to 185° (to be thrown away)	11	11	10
Carbolic acid distilling below 190°	48	45	45
" " " 195° to 196°	13½	17½	17½
Solidifying-point of these = 61½ to 62½ per cent.	15°	18°	16¾°

One thousand gall. of carbolic oil from Manchester tar yield about 50 gall. crude carbolic acid.

German gas-tar, according to Häussermann (*Ind. d. Teerfarbstoffl*, p. 17), on an average yields from 5 to 6 per cent. phenols; but according to Kraemer (*J. Gasbeleucht.*, 1891, p. 225) only 2 per cent. phenol and its homologues. Lunge and Schmid (*Chem. Ind.*, 1887, p. 337) found in coke-oven tar from Hoffmann-Otto ovens 2·23 per cent., in the tar from modified bee-hive ovens, 6·93 total tar-acids.

Of course, in working up the tar, only the phenol and the cresols are recovered as such; the higher homologues, from the xylenols upwards, for which there is up to the present no special use, are left in the heavy oils, where they contribute their share in the impregnating and disinfecting action of those oils.

Julius Rütgers (*Chem. Ind.*, p. 282) states that in his (numerous) factories there is recovered 0·2 per cent. crystallized carbolic acid and 0·3 per cent. cresols.

South-German gas-tars yield, according to Stohmann (Muspratt's *Chemie*, 3rd ed., vi., p. 1184), 0·33 per cent. crystallized carbolic acid, 0·48 liquid carbolic acid (containing a little cresols), and 3·2 per cent. cresol (containing a little phenol); according to Köhler (*Karbolsäure und Karbolsäurepräparate*, p. 97), 0·3 per cent. crystallized carbolic acid (fusing-point 38°) and 0·5 per cent. cresols.

North-German gas-tars, according to Kraemer (*J. Gasbeleucht.*, 1887), yield 0·35 to 0·50 per cent. phenol and 0·60 to 1·20 per cent. cresols. From German coke-oven tar Greiff obtained 1·37 per cent. pure phenol. From a mixture of gas-tar and coke-oven tar, Heusler (*Chem. Technol.*, Leipzig, 1905, p. 188) obtained 0·40 per cent. phenol and 1·13 per cent. cresols.

The yield of phenols from gas-tar has been mentioned *supra*, pp. 505 *et seq.*, from coke-oven tar, pp. 147 *et seq.*, from blast-furnace tar, p. 177.

Cresol obtained synthetically.

Kalle & Co. obtained in 1894 a German Patent, No. 81484, for the synthetical production of metacresol from naphthalene. The trisulphonic acid derived from the *m*-naphthalene disulphonic acid, with a sulpho-group in the substituted benzol remainder, when fused with caustic alkalies at 150° to 300°, furnishes metacresol quite smoothly, with intermediate formation of *m*-oxytoluene acid.

Methods for examining Carbolic Oil (Middle Oil) and Carbolic Acid of various Grades.

A. Examination of the Middle Oil.[1]—The middle oil, as it comes from the tar stills, ought to have the following properties:—

Specific gravity at 15° not below 1·0. On distillation it ought to yield up to 260° at least 90 per cent. It should contain not below 30 per cent. naphthalene. After separating the naphthalene the specific gravity should be 0·99 to 1·01; boiling-point up to 250°; percentage of bases 5 per cent., of phenols 25 to 35 per cent. The phenols, after removing the water, should commence boiling at 180° and go on till 210°; at 190° at least 25 per cent. of them should have passed over.

The examination of the *middle oil* comprises the establishment of the boiling-points, of the specific gravity of the raw oil, of the percentage of naphthalene, of the boiling-point and specific gravity of the oil after removing the crystals, of the boiling-point of the naphthalene, of the percentage of phenols and bases in the oil separated from the naphthalene, all of which tests are made as described *infra.*

For estimating the *naphthalene*, 0·5 to 4·0 kg. of the middle oil, previously liquefied and well mixed, is allowed to stand for twenty-four hours, with frequent stirring. The crystals separated during that time are freed from the mother-liquor by suction, then pressed between canvas or filtering-paper until they have no more an oily touch, and weighed. The *boiling-point of the naphthalene* is ascertained by distilling 100 g. of the pressed naphthalene in a copper still, and collecting the fractions coming over, degree by degree, in small porcelain dishes in which they are weighed.

Carbolic oil and the *naphthalene oils* are examined by the same methods as those just described for middle oil.

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[1] The following prescriptions are given by Dr Köhler, in the German edition of this book of 1912.

For *estimating the total phenols*, 100 c.c. of the oils are thoroughly shaken up in a graduated cylinder with 100 c.c. caustic-soda solution of sp. gr. 1·1, and the volume is read after the two liquids have clearly separated. Each cubic centimetre of the lower layer (the caustic-soda solution) over the original 100 c.c. is calculated = 1 per cent. of phenols. For a more exact estimation, the caustic-soda solution is carefully drawn off from the oil, then evaporated on a water-bath until no more turbidity is caused by an addition of water; after cooling down, the liquor is acidified by hydrochloric acid, and the phenols are separated by salting out. Their volume is measured, and here also each cubic centimetre calculated as 1 per cent. The final result is obtained by taking the mean of both operations.

In order to *examine the crude phenol for its yield of crystallized phenol*, at least 500 c.c. of the carbolic oil is extracted by caustic-soda solution of sp. gr. 1·1, and the alkaline solution heated on a sand-bath in a current of steam, until the liquid distilling over shows no more milky turbidity, and is free from smell and taste. The phenols are precipitated by carbonic acid, or by dilute sulphuric acid and saturated solution of sodium chloride; they are once washed with water, and carefully separated from it.

The *solidifying-point of the crude phenol* is ascertained by the "English method" worked out by Lowe. According to Kraemer and Spilker (*loc. cit.*) it is carried out in the German factories as follows:—One hundred c.c. of the crude phenol are placed in an ordinary fractionating-flask of a capacity of 150 c.c., the side-tube of which is by a perforated cork connected with a cooling-pipe 500 mm. long and of 10 mm. internal width. A thermometer is put on, and to begin with the water is expelled by heating and collecting in a 25 c.c. cylinder, divided into single cubic centimetres. The water is considered as completely driven off, when in this cylinder 10 c.c. of oil (carbolic acid) has collected *underneath* the water. Experience has shown that this oil can be assumed to be a mixture of 50 per cent. water and 50 per cent. carbolic acid. If, however, the oil floats *at the top* of the water, it is light tar-oil, and proves that the sodium-phenolate solution has been incompletely separated on the purification of the light oil or carbolic oil, or that the sodium-phenolate solution has not been sufficiently "steamed clear." If care is taken to avoid losses by imperfect cooling, the water can be pretty quickly driven off by catching the distillate at first in a two-litre flask, in which the cooling-pipe goes down to the belly, and heating until the temperature has risen from 100° to 150°. Since it is very important that the distillate now coming over should be absolutely free from water, which very much depresses the solidifying-point of the carbolic acid, the cooling-pipe of the fractionating-flask must during the distillation be warmed up by a special flame in its whole length, but more especially on its upper side, and in the place where it is connected by the cork with the side-tube of the flask until no more droplets of water are visible in those places; or else the cooling-pipe is exchanged for a fresh, dry pipe at the moment when no more water appears. In the same way also the neck of the flask between the side-tube and the thermometer cork must be warmed up in order to remove any water condensed there. This can be done without fear of losses, since the large surface of the two-litre flask, serving as receiver, condenses the water quickly and completely. Now the distillation is interrupted, the contents of the receiver are emptied into the above-mentioned 25 c.c. cylinder in which now the volume of the oils distilled over will amount to 7 or 8 c.c., and the distillation is continued until exactly 10 c.c. of oil has passed over. Now the receiver is changed, and a 100-c.c. cylinder, also divided into single cubic centimetres, is put on. The distillation must now be carried on so slowly that the distillate arrives *cold* in the receiver, in which 62·5 c.c. are collected. The residue remaining in the flask is worthless for the manufacture of carbolic acid and cresols.

The 62·5 c.c. obtained are utilized for ascertaining the solidifying-point, in the following way:—The cylinder is placed in a vessel, and by the assistance of ice cooled down rather below the solidifying-point expected. Now, by means of a correct thermometer, divided into tenths of a degree C. (the scale of which begins at 15 cm. above the mercury bulb, and goes from +10° to +40°), a tiny crystal of phenol is introduced, and stirred up, whereupon the crystallization soon sets in.

During the solidification of the whole the temperature rises. As solidifying-point we must take the highest point reached, at which the mercury remains stationary at least for a minute. In the case of crude phenol of good quality that point ought to be between 15°·5 and 24°.

For acquiring good practice in this work, mixtures are made of various contents of pure crystallized carbolic acid and of cresols (preferably tar-cresol, that is a mixture of the three isomers, *supra*, pp. 772 *et seq.*), the solidifying point of which has been previously ascertained. Mixtures of phenols with *pure* cresols (ortho-, para-, and metacresol), such as Lunge and Zschokke (*Chem. Ind.*, 1885, p. 6) have examined for their fusing points, do not give correct results, since (as pointed out by Lunge himself) the cresylic acid of coal-tar contains all three isomers, but in various proportions.

Another process, applied at an English factory, is described in *Chem. Zeit.*, 1884, p. 1338, but does not seem to be employed at any other place.

In order to *estimate the amount of bases* in middle oil, 100 c.c. of the oil, from which the phenols have been removed, is shaken up with 30 c.c. of dilute sulphuric acid (20 per cent. of H_2SO_4 + 80 water), and after settling down the increase of the volume of sulphuric acid is read off. By evaporation, as described *supra* for the estimation of the phenols, and cautious precipitation with caustic-soda solution of sp. gr. 1·40, applied in large excess, a controlling-experiment can be made.

If the object is to ascertain the percentage of the *pyridine bases*, suitable for denaturing alcohol, the bases precipitated as just described, together with the caustic-soda solution, are quantitatively put into a distilling-flask, a cooler is attached, and the distillation carried on until the distillate no more tastes of pyridine. The distillate, the volume of which will be about 50 c.c., is brought up to 200 c.c. by adding absolute alcohol, and to 10 c.c. of this mixture is added 2 c.c. of a saturated solution of cadmium chloride in water. After standing for twenty-four hours, the white crystals of the cadmium double salt formed are collected on a weighed filter, dried at 100° up to a constant weight, and weighed. 100 parts of these = 45 parts pyridine bases.

Commercial Forms of Carbolic Acid and the Cresols.

The designation "Carbolic Acid" is not confined in the chemical trade to a definite chemical individual, C_6H_5OH, but it is also used for the cresols, and their mixture with phenols; nay, even for crude tar-oils, containing a certain percentage of these phenols, together with a large quantity of impurities.

The commercial products belonging to this class are:—

(a) *Crude Phenol* or *Crude Carbolic Acid.*—This product is brought into the market principally from England. In the cold it forms a paste of crystals. If 50 per cent. are distilled off, the distillate at 15° yields crystals of phenol, which distinguishes it from crude cresol (so-called 100 per cent. liquid crude carbolic acid).

(b) *Crystallized Phenol.*—In the purest state it is a white, translucent mass of crystals, fusing at 40° to 42° and boiling at 183° to 184°. On fusion it forms a colourless liquid, of strong refraction, possessing a peculiar, not disagreeable, smell. Sp. gr. at $15° = 1{\cdot}066$. Soluble in 15 parts water at the ordinary temperature.

The products sent into the market under this designation show fusing-points from 42° down to 32°, since this point is strongly affected by very slight quantities of moisture and of cresols.

(c) 100 *per cent. Liquid Crude Carbolic Acid, Dark.*—A mixture of strong, sometimes nearly black colour, soluble in caustic-soda solution either clear or muddy, consisting principally of a mixture of the three isomeric cresols, but containing also considerable quantities of phenol, as well as some xylenol and more highly methylated phenols. It generally begins to boil at 185°, going on till over 210°. It serves for coarse disinfections, as well as for the preparation of purer articles, such as those enumerated in the following.

(d) 100 *per cent. Liquid Carbolic Acid, Clear* (German Pharmacopœia).—A liquid of yellow up to brown colour, of narrower boiling-point limits than the preceding, occurring in the trade either in the clear or in the muddy state. It is principally applied for pharmaceutical purposes.

(e) *Pure Cresol.*—A clear liquid, boiling from 185° to 205°, free from hydrocarbons, containing only traces of phenol and of more highly methylated products, consisting essentially of the three isomeric cresols. Also sold by the designation of *Schering's Tricresol.*

(f) *Technical Metacresol.*—A liquid of mostly yellowish colour. In the trade there are two qualities of it. One of these boils at 199° to 204°, and contains very little orthocresol, about 58 to 60 per cent. metacresol and the remainder paracresol. It is used in Germany for preparing "Liquor cres. sap." The second, more valuable quality boils at 202° to 204°, looks like the preceding, but is free from orthocresol and contains 88 to 90 per cent. metacresol.

(g) *Crude Commercial Carbolic Acid,* 25 to 30 per cent., or 45 to 50 per cent., etc. Consists of tar-oil fractions with a corresponding percentage of cresols and homologues, obtained in the working-up of the crude oils, or prepared by mixing.

Testing of Crude Carbolic Acid.

The properties of crude carbolic acid have been mentioned, p. 785.

C. Arnold and G. Werner (*Apoth. Zeit.*, 1905, p. 925; *Chem. Zeit. Rep.*, 1905, p. 381) give the following reactions for *distinguishing phenol and cresols.* Mix 10 c.c. of the aqueous solution, with caustic-soda solution, alcohol, and 1 drop aniline. Shake up, add 5 or 6 drops hydrogen peroxide, shake again, and add 12 drops of a solution of sodium hypochlorite. The colour reactions are then as follows:—Phenol yields a red colour, passing over into yellow; ortho- and metacresols, violet, at once changing into green; paracresol, purple red, quickly vanishing. The latter is distinguished from phenol and the other cresols in this way. Dissolve 2 drops (if necessary, after liquefying) in 3 c.c. concentrated sulphuric acid and add a trace of potassium nitrite; then *p*-cresol yields a dark red, but phenol, *o*- and *m*-cresol and tricresol an emerald green colour. With ferric chloride *o*-cresol yields a blue colour, rapidly turning green; *m*-cresol and phenol, purple; *p*-cresol, blue.

The *percentage of phenols in crude* carbolic acid can be *approximately* tested by shaking it up in a graduated tube with twice its bulk of 9 per cent. caustic-soda solution, added gradually. This is the usual process; that of Hager (employment of an alcoholic solution of potash; Wagner's *Jahresber.*, 1872, p. 675) is less used. The volume of the neutral oils (which may be at the top or at the bottom) is now read off. The separation of the oily and aqueous layers becomes more accurate if (as first proposed by Hager) a quantity of petroleum spirit is added in equal volume to that of the tar-oil; of course this volume must be deducted. This or any similar test cannot possibly be accurate, because the alkaline solution, especially if it be somewhat concentrated, dissolves indifferent oils and naphthalene. A check upon the reading of the volume of the neutral oils is: saturating, in a graduated tube, a measured portion of the alkaline liquor with hydrochloric acid and reading off the volume of the phenols separated.

Beckurts (*Arch. Pharm.*, 1886, xxiv., p. 572) states that the phenols will dissolve about as much water as the water will dissolve phenols, and even prefers, for *crude* carbolic acid, this test to Koppeschaar's (see p. 798).

The following prescription for testing crude carbolic acid was drawn up by Charles Lowe, in the first instance as an instruction to those tar-distillers who supplied him with their products, and is followed at most English and some Continental works. The sp. gr. should be between 1·055 and 1·070. One thousand fluid grains (or, say, 200 c.c.) of the oil are distilled in a retort, without any special condensing-apparatus, and the liquid passing over is collected in graduated tubes. Water first distils, and is followed by an oily fluid. When 100 fluid grains of the latter have been collected, the receiver is changed. The volume of the water is then read off. If the oily liquid floats on the water, it contains light tar-oil. It should be heavier than water, in which case it may be regarded as hydrated acid containing about 50 per cent. of real carbolic acid. The next portion of the distillate consists of anhydrous acid; and when it measures 625 g. the receiver is again changed. The residue in the retort consists wholly of cresylic acid and still higher homologues of carbolic acid. The 625 grains measure of anhydrous carbolic acid contains variable proportions of carbolic and cresylic acids. These may be approximately determined by ascertaining its solidifying-point (*vide supra*, p. 782) which should be between 15°·5 and 24° C.

Having ascertained this temperature, a mixture of carbolic and cresylic acids is made in such proportions as to have the same solidifying-point. This must be adjusted by trial, or a number of standard specimens may be prepared.[1] The exact point of solidification can be observed more exactly if a minute fragment of crystallized carbolic acid be added, to induce the commencement of the change of state: or the sample may be solidified and the liquefying-point noted. As excess of cresylic acid prevents crystallization, it is evident that in some cases a second fractional distillation should be resorted to, the process being arrested when the thermometer rises to 190°.

We may here mention Tidy's and Abel's methods (pp. 698 and 701) for estimating the quantity of "tar-acids" in creosote oil.

Dr Weyl, of Mannheim, tests crude carbolic acid by a caustic-soda solution of sp. gr. 1·263 to 1·297. Stronger alkali extracts substances whose sodium compounds are insoluble in the mixture of liquids, and are precipitated as a heavy layer between the oil and the sodium-phenate solution. These substances (which have not yet been examined) belong to the heaviest constituents of coal-tar.

According to Watson Smith, cresol retains less water of hydration than phenol; hence a superior quality of crude carbolic acid, containing less cresol, gives off more water than an inferior. In the former case up to 16 per cent. of water is found.

O. Bach[2] estimates water and phenol in one and the same sample of crude carbolic acid. Fifty c.c. of the acid to be tested are distilled in a retort until solid hydrocarbons begin to deposit in the condenser. The distillate is received in a wide burette, holding 100 c.c. and graduated in $\frac{1}{8}$ c.c., which has a glass tap fused on to its lower end. In this burette is previously placed a saturated solution of common salt, about 25 c.c. in volume, and its level is read off exactly. If the carbolic acid be free from water, the distilled oil separates clearly from the salt solution; but if it be aqueous, the oil with the water and brine form a kind of emulsion; by agitating, however, the two layers will quickly appear distinct. The increase in volume of the brine directly indicates the quantity of water contained in the crude acid. Before estimating the phenol, the brine is removed by means of the glass tap. The burette is then filled up to the zero-mark with a caustic-soda solution of sp. gr. 1·26, and, after closing with a cork, is vigorously shaken and allowed to settle. If the burette was quite clean and especially free from grease, the oil will have completely separated after half an hour, and its level can be observed. The difference from the volume formerly noted at once gives the amount of phenols.

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[1] *Cf.* (p. 277) the experiments made by Lunge and Zschokke on the fusing-points of mixtures of pure phenol and pure paracresol. Since "cresylic acid" contains all three isomeric cresols, the indications furnished by Lowe's prescription must be of a very rough character.

[2] *Chem. Zeit.*, 1882, p. 989.

Toth[1] shakes up 20 c.c. crude carbolic acid with 20 c.c. caustic-potash solution of sp. gr. 1·25 to 1·30, allows to stand for half an hour, and dilutes with water up to 250 c.c., whereupon the tarry constituents of the crude acid separate and are removed by filtration. The residue is washed with tepid water till the reaction has ceased to be alkaline; the filtrate and all the washings are collected and diluted to 3 litres. Fifty c.c. of this solution are taken out, and to this is added 150 c.c. of Koppeschaar's bromine solution (see below), and 5 c.c. of concentrated hydrochloric acid. The mixture is shaken up now and then for twenty minutes, 10 c.c. solution of potassium iodide is added; and, after standing at most five minutes, starch solution is added, and the free iodine titrated with sodium thiosulphate (see p. 799).

This method cannot be accurate, as crude carbolic acid contains a large amount of cresols, which combine with much less bromine than phenol proper, as first shown by Kleinert.[2] Hence Stockmeier and Thurnauer[3] modify the method in the following, at the same time more expeditious, way. They dissolve 1·5 or 2 g. of crude carbolic acid or 1·0 g. of strong carbolic acid in three times its volume of 30 per cent. caustic-potash solution, by shaking for five or ten minutes in a small flask; this they dilute to a litre, whereupon the hydrocarbons separate very well at the bottom or the top of the aqueous liquid. Of the latter a little over 100 c.c. is filtered, and two portions of 50 c.c. each are mixed in a stoppered flask with 100 c.c. of a solution of 2·517 g. sodium bromate and 9 or 10 g. sodium bromide in a litre, together with 5 c.c. strong hydrochloric acid; after standing for ten minutes 15 c.c. of a 12·5 per cent. KI solution is added, and the whole is titrated with sodium thiosulphate. At the end of the titration, together with starch solution, a little chloroform is added, which prevents the tribromphenols from curdling and thus enclosing some iodine. The presence of aniline and pyridine bases has but little influence.

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[1] *Fresenius's Zeit.*, vol. xxv., p. 160.

[2] *Z. anal. Chem.*, 1884, p. 1.

[3] *Chem. Zeit.*, 1893, pp. 119 and 131.

The same authors examine the phenols separately by extracting them with caustic-potash solution, removing from this solution all hydrocarbons by shaking with ether, precipitating the phenols with dilute sulphuric acid, and distilling them off by means of open steam. The distillate is saturated with NaCl, and the phenols are extracted by ether. The latter is driven off again, and the pure cresols are fractionated: 1st, up to 198° or 202°; 2nd, up to 240°; 3rd, above 240° C. Each fraction is separately titrated with bromine, and to reduce the figures to the true percentage of cresols they must be multiplied for the first fraction by $\frac{510·63}{444·44}$, for the second by $\frac{510·63}{x}$, where x denotes the total quantity of bromine calculated for 100 g. phenol. See, however, later on, the statements of Ditz and Cedivoda, who declare the principle of this analytical method to be erroneous.

Vaubel[1] pointed out that paracresol does not fix three, but only two atoms of bromine; Stockmeier and Thurnauer contend[2] that this does not affect their method and at most proves that their carbolic acids had contained little or no paracresol [?].

The *percentage of water* in phenol, according to Vulpius,[3] can be approximately tested by adding olive oil. Carbolic acid, free from water or containing but little water, can be mixed with many times its own volume without becoming turbid. The more water it contains, the less oil it will take without becoming turbid. Four volumes of crude carbolic acid containing not much above 10 per cent. water will give a clear mixture after being well shaken up with 4 parts of olive oil; a fifth part of oil will cause strong turbidity.

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[1] *J. prakt. Chem.* [2], xlviii, p. 74.

[2] *Chem. Zeit.*, 1893, p. 404.

[3] *Wagner-Fischer's Jahresber.*, 1884, p. 494.

Riesenfeld (*Chem. Centr.*, 1902, ii., 627) estimates the percentage of water in phenol by the electric conductivity of a solution of potassium iodide in the product to be tested.

Casthelaz[1] gives the following notes on the testing of crude and impure (liquid) carbolic acids:—"Crude carbolic acid" is a dark brown or black fluid, containing phenol, cresol, saponifiable oils, non-saponifiable oils, naphthalene, water, and ammonium sulphhydrate. Its percentage in crystallizable phenol is estimated by Lowe's method (*cf.* p. 787); "crude carbolic 60 per cent." means an acid which by Lowe's test indicates 60 per cent. of real phenol.—"Liquid carbolic 100 per cent., 95 per cent., 50 per cent." (not to be confounded with "liquefied pure carbolic acid," *cf.* below) mean articles containing the above percentages of cresol, for those acids do not contain more than traces of real (crystallizable) phenol. They have a more or less unpleasant smell, due to sulphuretted hydrogen, ammonium sulphhydrate, or organic bases. These sulphur compounds are easily detected by shaking up with water and adding subacetate of lead, which produces a more or less abundant black precipitate of lead sulphide. The sulphur compounds can be removed from phenol by agitating it with a solution of sodium bisulphite; the latter is changed into thiosulphate (Casthelaz's patent, 1881). The more or less deep colour of liquid carbolic acid depends upon the washings practised with the crude acid before redistillation. The more bases have been left in it, the darker the acid will turn with age. —The liquid carbolic acids at 95 and 90 per cent. contain 5 or 10 per cent. of water; "liquid carbolic acid 50 per cent." is an artificial compound, which appears in the market only in times of scarcity. It ought to contain 50 per cent. cresylic acid and saponifiable oils, 40 per cent. heavy and light, not saponifiable tar-oil, and 10 per cent. water; but articles have been sold under that name by English and German manufacturers which did not even contain 30 per cent. saponifiable oils.

Instead of the ordinary soda test, Casthelaz proposes the following tests:—

1st. Shake up 50 c.c. liquid carbolic acid with 50 c.c. of water. The volume of the carbolic acid should remain almost the same; if not, it contains alcohol, glycerin, carbolate of soda, etc.

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[1] *Bull. Soc. Chim.*, vol. xlii., p. 574.

2nd. Shake up 50 c.c. of the liquid carbolic acid with 50 c.c. of sulphuric acid, diluted with 50 per cent. water. Any slight diminution of the volume of carbolic acid corresponds to its percentage of water. If the diminution of volume is considerable, there is probably carbolate of soda present; and the insoluble upper layer indicates the quantity of cresylic acid and other saponifiable products.

3rd. 100 c.c. liquid carbolic acid is mixed with 100 c.c. caustic-soda solution of sp. gr. 1·38, and diluted with water up to 1 litre. This will separate the non-saponifiable products; the naphthalene floats at the top in the solid state, and can easily be collected and weighed.

4th. 100 c.c. are distilled in a tubulated retort, the thermometer reaching down to within 1 cm. ($\frac{3}{8}$ in.) from the bottom. Notice is taken, 1st, of the water coming over before the cresol; 2nd, of the oily product distilling between 182° and 190°, and consisting mainly of phenols; 3rd, of the percentage distilling between 190° and 205°, = cresol; 4th, of the residue remaining in the retort.

The test of the German Pharmacopœia for "90 per cent. crude carbolic acid" is as follows:—Shake 9 volumes of caustic-soda liquor of sp. gr. 1·079 to 1·08 very thoroughly with 1 volume of crude phenol and allow to settle perfectly; the portion remaining insoluble, which floats on the top and which is liquid or semiliquid, ought not to exceed 10 per cent. by volume. The product reprecipitated from the alkaline solution by adding hydrochloric acid, in the case of a good article (not containing an excess of cresol), should be soluble in at most thirty parts of water.

Hager tests crude phenol of no less than 85 per cent. by shaking 10 c.c. with 20 c.c. glycerin, heating gently, shaking again, and allowing to settle for six or ten hours. The lower, brighter layer is a solution of the phenols in glycerin; the upper, darker one consists of the impurities.

Naphthalene in crude carbolic acid is estimated by Muter (*Chem. Centr.*, 1890, i., p. 840) by shaking 50 c.c. of the sample with 200 c.c. of a 10 per cent. solution of caustic soda, which leaves the naphthalene behind. It is filtered, washed with water, pressed, and weighed. [Of course this process holds good only for the very exceptional case that no tar-oils are present, which would keep part of the naphthalene dissolved.]

Seiler (*Schweiz. Wochensch. f. Pharm.*, 1892, p. 365) heats 100 g. crude carbolic acid with 100 g. milk of lime (1 : 5) for an hour on the water-bath, with stirring, adds 100 c.c. water, and filters after cooling. In so-called 40 to 45 per cent. commercial carbolic acid he found only 3 to 5 per cent. phenols. [This method is utterly worthless, as was also shown by Klisch (*Pharm. Zeit.*, 1892, p. 650) and Roos (*ibid.*, p. 666).]

Lohmann[1] extracts with caustic-soda solution, and afterwards the non-saponifying oils with petroleum spirit.

Schacherl[2] extracts several times with caustic-soda solution of sp. gr. 1·1, dilutes the solutions with the same volume and water, and distils until the distillate is quite clear and free from oil. The residue, after cooling, is acidulated with HCl and again distilled. The water separating from the distillate is distilled over again, till quite clear, and the phenol separated from all these solutions by sodium chloride. [This is not altogether an exact method.]

C. E. Smith[3] describes a somewhat complicated process for applying the bromine method to the examination of crude carbolic acid, which cannot give very accurate results.

Schryver[4] points out that all bromine or iodine methods must be wrong in the presence of hydrocarbons reacting upon Br or I. His own method is founded on the evolution of NH_3 from sodium amide by hydroxyl compounds:

$$NaNH_2 + C_6H_5OH = NaOC_6H_5 + NH_3$$

About 1 g. of powdered sodium amide is washed with pure benzene (free from thiophen) and is then placed, together with 50 or 60 c.c. pure benzene, in a wide-necked flask, connected with a reflux-cooler, a drop-funnel, and an aspirator. It is heated to boiling on a water-bath, and the NH_3 adhering to the amide is removed by aspiration. Now the sample to be tested, dissolved in 6 parts pure benzene and completely dried with fused sodium acetate, is run in through the drop-funnel, a receiver with 20 c.c. normal sulphuric acid having been interposed between the apparatus and the aspirator. The boiling is continued, air being always aspirated through, and the funnel being well rinsed with benzene, until all NH_3 is evolved, which takes about an hour and a half. It is indispensable that the apparatus should be absolutely dry. By titrating the acid in the receiver, the phenol can be estimated to + 2 per cent. In mixtures of phenol and cresol the "hydroxyl number" thus found permits of calculating the mutual proportion of both to about 10 per cent. In order to estimate the *water*, the phenols are dissolved in benzene, dried with dehydrated acetate, and the phenol estimated as above.

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[1] *Chem. Zeit.*, 1892, p. 365.

[2] *Pharm. Centralhalle*, 1892, No. 2.

[3] *Amer. J. Pharm.*, 1898, p. 369; *Chem. Zeit.*, 1898, p. 230.

[4] *J. Soc. Chem. Ind.*, 1899, p. 553.

Fischer and Koske, in *Süd. Chem. Zeit.*, 1903, No. 21, describe a number of samples of "crude carbolic acid" which consisted mainly of cresols, as proved by fractionating, etc.

Recently crude carbolic acid has sometimes been found adulterated with the phenoloid substances from blast-furnace tar, which chemically are much nearer to the complicated phenols of wood- and lignite-tar. Possibly their antiseptic properties equal those of the coal-tar phenols, but at all events they should not be added to these without informing the buyer thereof.

Kraemer and Spilker (Muspratt's *Chemie*, viii., p. 58) establish the technical value of crude phenol as follows:—200 g. of the crude phenol are distilled according to the method of Lowe (*supra*, p. 787), making two fractions. The first of these ("first runnings") should, beside the water, contain 20 c.c. oily matter; the second consists of the following 125 c.c. Of this second fraction the solidifying point is established, as described *supra*, p. 782; also the clear solubility, by shaking up 1 part oil with 4 parts of a 10 per cent. solution of potassium or sodium hydrate; this ought to produce a clear solution, not becoming turbid when diluted with water. In order to completely separate the water in the first runnings, these are mixed in a graduated cylinder with the three- or fourfold quantity of benzol.

Church and Weiss (*J. Ind. Eng. Chem.*, 1914, p. 396) tried the methods for proving the presence of *paraffins* in coal-tar creosote. The dimethylaniline method of Chapin is not reliable, but good results are obtained by Bateman's method of treating the creosote oil with fuming sulphuric acid which dissolves the real creosote, and leaves the paraffins behind. Creosote oil from coke-oven tar was found to contain no paraffins; gas-tar contains 0·2 to 6·4 per cent. of paraffins, the lowest percentage occurring in the tar from horizontal gas-retorts. Water-gas creosote-oils contain from 0·4 to 14·2 per cent. paraffins.

Cloukey (*J. Ind. Eng. Chem.*, 1915, p. 923) describes the examination of creosote-oils for carbon and dirt by the Davis spot tests.

Examination of Pure Phenol and Cresols.

The properties of pure phenol have been described *supra*, pp. 268 *et seq.* The "pure carbolic acid" of the trade shows fusing-points, ranging from 42° down to 32°, which are strongly influenced by the presence of small quantities of water and of cresols (Lunge and Zschokke, *Berl. Ber.*, 1882, p. 2201). Synthetically produced phenol is also found in the trade (see p. 764); its properties in all essential points are the same as those of the phenol extracted from coal-tar.

Ordinary commercial "pure" carbolic acid may contain traces of fixed substances—compounds of sodium, calcium, copper, lead, etc., but never more than in most minute quantities. More usually there are present small quantities of higher-boiling phenols, of substances which cause the development of a red or yellowish-brown colour (pp. 766 *et seq.*), and of *water*. Crystallized phenol may contain as much as 5 per cent. water; only when containing 7 per cent. and upwards of water, carbolic acid remains liquid at ordinary temperatures. Water lowers the fusing-point of phenol, but it increases its solubility (perhaps the statements of Allen, ascribing to phenol a greater solubility than that found by all other observers, p. 270, may be explained in this manner). Even 1 per cent. of water may be recognized by shaking the phenol with its own volume of chloroform or ether, which in that case will produce a milky liquid. The quantity of water can be approximately tested by the increase in volume of a concentrated solution of sodium chloride or calcium chloride, as has been described above in connection with the testing of crude carbolic acid. The quantitative estimation of the water can be exactly performed by mixing the phenol with about five times its weight of finely levigated lead oxide, and drying at 70° or 80° till the weight is constant, or by Schryver's method, p. 793; *cf.* also pp. 788 and 790.

Very important for judging of the quality of "pure carbolic acid" is the examination of its *fusing-point*, or preferably its *solidifying-point*.

A further examination has to be made of the *clear solubility* in 10 per cent. *caustic-soda solution*, and in *water*; for pharmaceutical purposes, also *metallic impurities* come into question, both such as come from the apparatus employed, and such as are added on purpose, *e.g.*, stannous chloride.

Fusing-point and Solidifying-point.—Methods for ascertaining this are described *supra*, p. 782.

Eger (*Pharm. Zeit.*, 1903, p. 210; *Chem. Zeit. Rep.*, 1903, p. 86) contends that the fusing-point of carbolic acid = 40° to 42° C., as demanded by the German Pharmacopœia, is decidedly too high. The purest obtainable phenol solidifies at 40·9, and its fusing-point is at most 0·1° higher. Hence the fusing-point should be put at the highest at 41°, better at 39° to 41°.

The higher-boiling phenols greatly lower the fusing-point of carbolic acid. This is most clearly proved by the experiments of Lunge and Zschokke (*cf.* p. 277), which prove such a lowering of the fusing-point, even when the second phenol is paracresol, whose fusing-point is as high as 32°·5. But since commercial carbolic acid contains even larger proportions of metacresol, which is liquid far below the ordinary temperature, the lowering of the fusing-point is far more considerable than would be indicated by those experiments. The reddish or brownish liquid collecting in the vessels where not absolutely pure phenol is kept mostly contains those higher phenols. Carbolic acid, free from these, even when containing several per cent. of water, after heating for some time in an open dish and cooling down in a desiccator over concentrated sulphuric acid, solidifies to a white crystalline mass, with a melting-point of about 30°; but if it contains a little cresol, etc., the residue is brown, and has a much lower melting-point, sometimes remaining liquid. Some authorities assume that these very substances cause the reddening of phenol by an oxidizing process (p. 271). They are also indicated by agitating phenol with three times its bulk of pure concentrated sulphuric acid, to which they impart a yellow, brown, or pink colour; also by forming a muddy mixture with glycerin, and by furnishing with bromine a product distinct from pure tribromophenol by not being crystalline, by being coloured, and by fusing below 90°. (*Cf.* also Allen's table of the differences in the behaviour of carbolic and cresylic acids, p. 275.)

Solubility.—Pure carbolic acid should dissolve completely in 4 vols. of 10 per cent. caustic soda or potash solution, forming a perfectly clear liquid which is not rendered turbid by addition of water. An even more delicate test is the solubility in water; 1 part pure phenol should dissolve in 15 parts of distilled water of 15° C. to a perfectly clear liquid.

When fused, pure phenol is as limpid as water and perfectly colourless, and on solidifying it should form a white or glassy translucent mass. But in course of time even the purest phenols turn red; *cf.* pp. 271 and 766.

Sulphur Compounds.—Crystallized carbolic acid ought in no case to contain any sulphur compounds, which impart to it a nauseous smell, and which can be detected by adding subacetate of lead (p. 772), or by boiling an alcoholic solution of the sample with lead hydroxide.

Liquefied pure carbolic acid—that is, pure phenol purposely liquefied by the addition of 10 per cent. water, alcohol, or glycerin—can be distinguished from "liquid carbolic acid," which essentially consists of cresols, etc. (p. 785), by its boiling-point (beginning at or below 100°, but quickly rising to 185° to 190°, whilst the last-mentioned article boils at 185° to 209°), by its solubility in water (the liquefied pure acid requires *at most* 18 parts of water to form a clear solution, while cresylic acid is not completely dissolved even by 50 parts of water), by the different properties of the bromine precipitates, and by all the other distinctive reagents mentioned (p. 275). Its percentage of pure phenol is determined by one of the methods described below.

Schlickum (*Pharm. Zeit.*, 1884, p. 794) founds a testing-method on the increase of volume produced in liquefied carbolic acid by shaking with its own volume of water. This method is accurate, but the measurement should be made very correctly, as a difference of 1 c.c. is = 8 to 10 per cent. of water.

Vulpius proposed another somewhat similar method which has been worked out in detail by Salzer (*ibid.*, 1886, No. 1). He also points out that, whilst anhydrous phenol gives a clear mixture with carbon disulphide, aqueous phenol yields a milky liquid, which requires all the more acid to clear it the more water the phenol contains. Later on (*Pharm. Centr.*, 1891, p. 153) Salzer described another test for liquefied carbolic acid: 10 c.c. must not give a permanent turbidity with 2·3 cm. of water; with more water, the sample must yield a turbid mixture which dissolves to a clear liquid with not less than 135 and not more than 140 c.c. water.

Small quantities of cresol are not indicated by these methods; *cf.* Beckurts (*Arch. d. Pharm.* [3], vol. xxiv., p. 580).

Eger (*loc. cit.*) states that liquefied carbolic acid should be tested as follows:—10 c.c. should at 15° not be rendered cloudy by adding 2·3 c.c. water, but by the further addition of 8 to 10 drops of water. This cloudy solution should form a clear solution by the addition of not less than 115 and not more than 135 c.c. of water.

The exact *quantitative estimation of phenol* is always made by precipitating it with bromine as tribromphenol, a reaction discovered in 1871 by Landolt. Tribromphenol forms white star-shaped groups of needles, of a peculiar smell, fusing at 95°, insoluble in water, acids, or somewhat dilute alcohol, but soluble in alkalis, ether, or absolute alcohol. Hence it is necessary to acidify the phenol or its solution in water or dilute alcohol, and to add bromine-water till the liquid has assumed a permanent yellow colour. It is best to heat the liquid till the precipitate fuses to an oil, and then to cool it; the precipitate thus solidifies to a cake, which is easily washed, dried, and weighed. If much cresol is present (which also gives a tribrom-derivative, though a liquid one), the precipitate will be a sticky mass. It is therefore not possible to separate phenol from cresol by this method. One hundred parts $C_6H_2Br_3(OH)$ correspond to 28·4 $C_6H_5(OH)$; and the quantity of bromine which indicates 1·000 phenol would indicate 1·106 cresol. As a *gravimetric* method, however, this test is not correct, for Weinreb (*Monatsh.*, 1885, p. 506) has shown that the precipitate is not $C_6H_3Br_3O$, but $C_6H_2Br_3OBr$; but the additional bromine in titrating sets iodine free from KI, so that Koppeschaar's volumetric method is exact after all. Beckurts (*Arch. d. Pharm.*, 1886, vol. xxiv., p. 561) confirms this.

The gravimetrical estimation of phenol by this method is, moreover, much hampered by the fact that the tribromphenol is rather volatile at 100°. But the formation of that compound can be turned to account for an accurate *volumetrical* estimation, which was first proposed by Koppeschaar (*Z. anal. Chem.*, 1876, p. 233). We here describe his method, which is still that which is most frequently employed. The liquids required are—

1st, a solution of sodium thiosulphate, exactly corresponding to a solution of iodine, containing 5 g. I per litre;

2nd, solution of starch;

3rd, bromine-water of such concentration that 50 c.c., after being decomposed with potassium iodide, require 18 to 20 c.c. of the thiosulphate solution;

4th, a solution of potassium iodide, containing 125 g. per litre.

Dissolve 4 g. of the sample of carbolic acid in water, and dilute up to 1 litre. Put 25 c.c. of this solution into a stoppered half-litre flask, fill it quickly up to the mark with bromine-water, close it and agitate for some time. Before adding the bromine-water, run 50 c.c. of the same into a small beaker, containing 5 c.c. of the potassium-iodide solution. After standing for half an hour, empty the contents of the half-litre flask into a large beaker, already containing 5 c.c. of the potassium iodide solution, and rinse the flask twice into the same beaker. Then titrate the liquids, both in the small and the large beaker, with the thiosulphate solution, adding some of the starch solution, but only towards the end of the operation, and read off, when the blue colour ceases to return after a few minutes.—We have thus employed 25 c.c. of the phenol solution (corresponding to 0·1 g. of the sample), we have added 475 c.c. bromine-water, and we have standardized 50 c.c. of the latter with a thiosulphate solution of the strength formerly indicated. If we call a the c.c. of thiosulphate required for the 50 c.c. of bromine-water, and b the c.c. of thiosulphate required for the excess of bromine in the 25 c.c. of the solution, the formula

$$(9{\cdot}5\,a - b)0{\cdot}61753$$

directly indicates the percentage of phenol in the sample.

Koppeschaar also mentions that, instead of bromine-water, a mixture of five molecules of sodium bromide and one molecule of sodium bromate may be employed. This mixture is obtained by adding to a solution of caustic soda an excess of bromine and evaporating to dryness. The resulting mixture of salts is redissolved, and, on adding hydrochloric acid, yields all its bromine in the free state:

$$5NaBr + NaBrO_3 + 6HCl = 6NaCl + 6Br + 3H_2O.$$

It is, however, not necessary to evaporate the original mixture to dryness; it is sufficient to boil the solution of bromine in caustic soda for some time. Allen[1] has proved that a boiled solution of this kind keeps its standard for a long time. He had himself formerly[2] proposed employing this solution in lieu of bromine-water, and obtaining its standard by calculation, by employing a standard solution of caustic soda for preparing the mixture; but this very indirect method introduces an element of uncertainty, and seems less trustworthy than Koppeschaar's original method, which is also preferred by Waller.[3]

It seems the most certain method to standardize the bromine-water with pure phenol itself. This has been recommended by Diacosa (*Rep. Anal. Chem.*, ii., p. 137); and is also employed by Allen in his last prescriptions for determining the phenol in carbolic soap (see below). Diacosa runs the aqueous solution of phenol into the bromine-water, and determines the end of the reaction by testing a drop of the clear solution with paper soaked in a solution of starch and potassium iodide. This plan was first proposed by Degener (*J. prakt. Chem.* [2], xvii., p. 390). Chandelon (*Bull. Soc. Chim.*, xxxviii., p. 69) uses the same indicator; but he employed the brominated caustic soda in lieu of bromine-water. These direct tests are quite incorrect, owing to the formation of tribromphenol-bromide (p. 798).

Beckurts (*cf.* above) proposes the following as the most certain way of testing. The solutions employed are:—

1st. A $\frac{1}{20}$ normal solution of potassium bromide, containing 5·939 g. KBr per litre.

2nd. A $\frac{1}{100}$ normal solution of potassium bromate, containing 1·6666 g. $KBrO_3$ per litre.

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[1] *J. Soc. Chem. Ind.*, 1884, p. 64.

[2] *Commercial Organic Analysis*, 1879, vol. i., p. 307.

[3] *Chem. News*, xliii., p. 153. The figures given by Allen for calculating the results, which were repeated in the first edition of the present work, are wrong. Every cubic centimetre of the thiosulphate solution used over and above 6·17 c.c. indicates 0·00157 g. impurities in 0·1 g. of the sample, or 1·57 per cent.

3rd. A solution of 125 g. potassium iodide per litre.

4th. A $\frac{1}{10}$ normal solution of sodium thiosulphate, containing 12·4 g. of $Na_2S_2O_3$, 5 aq., per litre, and equal to 0·008 g. bromine or 0·00156 g. phenol per cubic centimetre.

This method is also recommended by Redman, Weith, and Brock (*J. Ind. Eng. Chem.*, 1914, p. 205).

Into a well-stoppered bottle put 25 to 30 c.c. of the solution of phenol (1 : 1000), add 50 c.c. each of the solutions of KBr and $KBrO_3$, then 5 c.c. concentrated sulphuric acid, and shake vigorously. After ten or fifteen minutes add [illegible] c.c. of the KI solution, and titrate the iodine which separates with the thiosulphate solution. This process is accurate whenever solutions of *pure* carbolic acid are to be tested, or mixtures from which such can be isolated, but it fails in the case of crude carbolic acid or other mixtures where cresol is present.

Moerk (*Chem. Zentr.*, 1904, ii., p. 1764) recommends as indicator in Koppeschaar's method chloroform in lieu of starch solution, the final reaction being sharper. S. J. Lloyd (*ibid.*, 1905, i., p. 599; *J. Amer. Chem. Soc.*, 1905, xxvii., p. 16) describes his special way of carrying out that method, by which he believes to attain an accuracy up to 0·1 per cent.

Olivier (*J. Soc. Chem. Ind.*, 1910, p. 79) declares Lloyd's criticism of Koppeschaar's method to be unfounded, and his method of estimating phenol to be inaccurate. Further modifications of Koppeschaar's method are described by Authenrieth and Beuttel (*Chem. Zentr.*, 1910, i., p. 1646); Telle (*J. Pharm. Chim.*, 1901, xiv., p. 389); Mascarelli (*Gazz. Chim. Ital.*, 1909, p. 180); Olivier (*J. Soc. Chem. Ind.*, 1910, p. 936); Versfeld (*Z. angew. Chem.*, 1915, ii., p. 592).

Since the higher-boiling phenols are much less soluble in water than real carbolic acid, or even insoluble, the direct application of Koppeschaar's method, as will be easily understood, yields very unsatisfactory results with creosote oils containing such higher phenols.[1] In this case the phenols may be dissolved in caustic soda solution, and this solution may be titrated with bromine-water in the presence of an excess of acid; but in the best case only approximate results can be thus obtained, especially since the calculating factor for the higher-boiling phenol is quite different from that for carbolic acid (see p. 798).

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[1] Cf. *Z. anal. Chem.*, xxiii., p. 1 (Kleinert).

Leube's colorimetric method, with employment of ferric chloride,[1] and Nietsch's method of converting the phenols into sulphonates of barium or lead and estimating those metals,[2] can evidently not yield any accurate results. The same holds good of the proposal of Carré, to convert the phenol into picric acid and estimate this colorimetrically.[3] Bader[4] makes a solution of not less than 20 g. phenol per litre, of which 50 c.c. is titrated with standard soda solution, employing as indicator a solution of the symmetrical trinitrobenzenes. The liquid must be completely colourless to begin with, and the end is shown by a reddish-yellow colour. This process can hardly yield satisfactory results.

Messinger and Vortmann[5] employ an iodometrical process. They dissolve 2 or 3 g. of phenol in at least 3 molecules caustic soda (in solution), dilute to 250 or 500 c.c., heat 5 or 10 c.c. to 60°, and add decinormal iodine solution until the liquid has turned strongly yellow, when on shaking a red precipitate of iodophenols is formed. The cooled liquid is acidulated with dilute sulphuric acid, diluted to 250 or 500 c.c., and 100 c.c. of this is titrated back with decinormal thiosulphate. Each 6 molecules of iodine used = 1 molecule phenol.

Korn[6] applies this process to the estimation of phenol in sewage.

Wake and Ingle[7] discuss the iodine values of the various phenols, which differ very much from one another.

Storch[8] gives a cryoscopic method for estimating water and orthocresol in crystallized carbolic acid, which can at the best yield only approximate results.

Keppler[9] proposed extending Koppeschaar's method to the estimation of pure cresols, starting on the assumption that they fix three atoms of bromine, which is quite wrong, as already pointed out by Vaubel,[10] and more in detail by Ditz and Cedivoda.[11] They show that metacresol with an excess of bromine forms a tetrabromide, whilst orthocresol fixes only two atoms of bromine. Up to the present, an accurate method for separating phenol and the three cresols does not exist. *Cf.* also Vaubel (*Z. angew. Chem.*, 1899, p. 1031) and Ditz (*ibid.*, p. 1155).

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[1] *Dingl. polyt. J.*, ccii., p. 308.

[2] *Wagner's Jahresber.*, 1879, p. 1036.

[3] *Comptes rend.*, 1891, p. 139.

[4] *Z. anal. Chem.*, 1892, p. 58.

[5] *Berl. Ber.*, 1890, p. 2753.

[6] *Z. anal. Chem.*, xxxiii., p. 552.

[7] *J. Soc. Chem. Ind.*, 1908, p. 215.

[8] *Berl. Ber.*, xxvii., referate p. 90.

[9] *Arch. Hyg.*, xviii., p. 51.

[10] *J. prakt. Chem.* [2], xlviii., p. 74.

[11] *Z. angew. Chem.*, 1899, pp. 873 and 897.

Muter[1] proves the presence of water in cresols by shaking the sample with three volumes of a saturated solution of sodium chloride. Anhydrous cresol absorbs about 5 per cent. of the latter; but if the cresol is already saturated with water, the volume of the salt solution is not changed.

Tocher (*Pharm. J.*, lxvi., p. 360) estimates phenols, in the absence of other oxidizable substances, by a decinormal solution of potassium permanganate. The solution of phenol (1 : 100) is mixed with an excess of sodium bicarbonate, the permanganate is added, and the whole boiled for a few minutes. After cooling, dilute sulphuric acid is gradually added till the reaction has turned acid; the liquid is warmed up and titrated back with decinormal oxalic acid. Each 0·01 g. pure C_6H_6O takes 29·78 c.c. decinormal $KMnO_4$.

Reuter (*Chem. Zentr.*, 1905, i., p. 1012) tests pure carbolic acid for the presence of phosphoric acid and tin salts; the former might have been added to prevent reddening, and the latter might have been taken up from the containing vessels.

Methods for estimating the Three Isomeric Cresols.

For this purpose Raschig (*Z. angew. Chem.*, 1900, p. 759) has worked out the following process:—Weigh off exactly 10 g. of the cresol mixture in a small Erlenmeyer flask. Add 15 c.c. of sulphuric acid, sp. gr. 1·38. Keep for an hour in a steam oven; then pour into a wide-necked litre-flask, cooling this on the outside under a water-tap; this will cause the sulphonic mixture to spread as a syrup on the sides of the flask. Put 90 c.c. nitric acid (sp. gr. 1·4) into the Erlenmeyer, shake it to dissolve the remains of the sulphonic mixture left therein, pour the whole quickly into the litre flask, and shake this vigorously till all the sulphuric acid is dissolved, which should be the case in about twenty seconds. Place the flask at once under a draught hood. Very soon a violent reaction sets in. The liquid boils vividly, red vapours escape, and oily drops of trinitrocresol separate. After ten minutes standing pour the contents of the flask into a dish already containing 40 c.c. of water, and rinse it with another 40 c.c. water. The trinitrocresol now solidifies, with escape of nitrous vapours. Leave all to cool for two hours, then squash the mass with a pestle and put it on to a vacuum filter. When the liquid portion has passed through, wash the filter with 100 c.c. water, dry at 95° to 100° and weigh, using a filter-paper of the same size as counterpoise. Such a test takes about five hours, and ten to twenty tests may be made at the same time. Ten g. pure metacresol in this manner gives exactly 17·4 g. of the nitro-product, and mixtures of all three cresols give exactly 1·74 part of the nitro-product for each part of *m*-cresol present. In the presence of less than 10 per cent. phenol this process is still quite accurate, but when more than 10 per cent. C_6H_6O is present, it does not work. Such mixtures are, however, not often found in commerce, and they would in any case be recognized by the boiling-points. Xylenols act in the same manner; in their presence the nitro-product does not properly solidify.

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[1] *Chem. Zentr.*, 1890, p. 840.

Raschig's process is exact up to 1 per cent., and as a method for practical working seems to fulfil all purposes, but it takes about five hours of work, wherefore Ditz (*Z. angew. Chem.*, 1900, p. 1050; see below) prefers the method worked out by him and Cedivoda (p. 805).

A discussion on the accuracy of Raschig's process has been carried on in 1908 by Eger (*Chem. Zentr.*, 1908, i., p. 405); Herzog (*ibid.*, p. 546); Raschig (*ibid.*, p. 973); Herzog (*ibid.*, p. 1214). *Cf.* also Fortmann in *Chem. Zeit.*, 1908, p. 118, who entirely approves of Raschig's process.

Russig and Fortmann (*Z. angew. Chem.*, 1901, p. 157) describe a similar process for estimating metacresol in mixtures of cresols which takes more time than the foregoing, but is claimed to yield more accurate results. Weigh 50 g. cresol in an Erlenmeyer flask. Add 150 c.c. sulphuric acid (1·84 sp. gr.), and allow to stand for one or two hours without applying outside heat. For nitrating employ a tubulated glass retort, holding 1 litre, placed on a sand-bath; connect its downward branch with a good chimney-draught, interposing a wash-bottle. Put 400 c.c. nitric acid (1·38 sp. gr.) into the retort, heat it up to 60° C., and remove the flame. Close the tubule of the retort by a perforated indiarubber stopper, through which passes the tube of a cylindrical drop-funnel. This must be wide enough to receive the neck of the Erlenmeyer when this is quickly reversed into the funnel, where it is left during the operation. Now allow the sulphonic acid to enter into the hot nitric acid, drop by drop, which should take one and a half or two hours. Much heat is developed, and copious nitrous vapours are given off. After standing for another twenty minutes, pour the contents of the retort into a roomy porcelain dish containing 200 c.c. water, and rinse the retort with another 200 c.c. of water. Allow to stand till the next day, squash the cake left in the dish with a porcelain spatula, and collect the trinitrocresol in a hardened filter on a vacuum pump. Another 200 c.c. water is used for rinsing the dish and the crystals. These are dried in a steam oven at 95° to 100° C., and weighed. In this way you obtain from perfectly pure *m*-cresol 175·6 per cent. of the trinitro-product, against 174·0 by Raschig's plan.

Already, in 1899 (*Z. angew. Chem.*, 1899, pp. 873, 879), Ditz and Cedivoda had worked out a volumetric process for estimating metacresol in a mixture of the cresols. To this they drew attention again in 1900 (*ibid.*, 1900, p. 1050), and they defend it also against an attack made upon it by Russig and Fortmann in their just-quoted paper in 1901 (*ibid.*, 1901, p. 160). Their process is based on the difference of behaviour of the isomeric cresols against a brominating mixture. It is claimed to give very accurate results in a short time, but it requires the *complete* absence of phenol and of xylenols; in this respect the process of Raschig or Russig has the advantage over it. Ditz and Cedivoda weigh off 1 g. cresol, dissolve in water with a little caustic soda, and dilute to 250 c.c. Of this solution they bring two samples of 25 c.c. each into stoppered bottles, add a sufficient quantity of Koppeschaar's bromide-bromate solution, then 10 c.c. of hydrochloric acid (1 : 1), shake exactly one minute, and add 20 c.c. of a 5 per cent. solution of potassium iodide. After standing one hour, the separated iodine is titrated with thiosulphate, the quantity of which corresponds to the bromine taken up. If you call the quantity of metacresol originally present x, the sum of ortho- and paracresol y, a the weight of cresols employed, and b that of the bromine absorbed, the two equations: $x+y=a$, and

$$\frac{3\text{Br}\,x+2\text{Br}\,y}{108.08}$$

allow to infer the quantity of metacresol to be

$$x=a-y=a-\frac{2.2195\,a-b}{0.7397}=\frac{b-1.4798a}{0.7397}.$$

The results are accurate up to 0·5 per cent.

Commercial Preparations made from Carbolic Acid and Cresol.

The widely extended use of carbolic acid and its homologues has led to their being produced in various forms, adapted to special purposes. We shall enumerate only those actually manufactured on a large scale, so far as they have not yet been mentioned before. They are almost exclusively disinfectants and preserving agents.

On the general demands to be made from cresol preparations, both for medical and disinfecting purposes, Kelhöfer (*Chem. Zeit.*, 1907, p 1028) has laid down the following rules:—

1. They must be perfectly clear, and clearly soluble in water, alcohol, ether, petroleum, petroleum spirit, benzol, chloroform, and glycerin.

2. They must contain at least 50 per cent. phenol and cresols, boiling up to 210°. This will be the case if 100 c.c., on being distilled in a fractionating flask, in which the thermometer bulb is about 1 c.m. below the side tube, and which is heated by a metal bath up to 210°, after adding a little common salt to the distillate, yield at least 45 c.c. cresol.

3. The cresol preparations serving for medical and veterinary purposes must have a neutral reaction, which will be the case, if a sample, agitated with five times its volume of sodium chloride solution, and filtered, is not coloured red by adding a few drops of phenolphthalein solution.

There are three groups of preparations made from carbolic acid and cresols, viz., 1st, such which make the phenols soluble by the action of a soap; 2nd, such where other means are employed for the same purpose; 3rd, solid products for various disinfecting purposes, whether soluble or insoluble.

I. *Carbolic Acid Soaps.*

Such preparations, as far as they are made from heavier tar distillates (creosote oil), have been described in Chapter VIII., pp. 658 *et seq.*, as tar-oil emulsions, going by the fancy names—*creoline*, *lysol*, *sapocarbol*, *etc.* They are not merely made from the heavier oils but also from "carbolic oil."

The German Imperial Board of Health has published the following prescription for a 5 per cent. solution of crude carbolic acid in soap: Dissolve 3 parts soft green soap in 100 parts hot water, and pour in 5 parts of crude (100 per cent.) carbolic acid, with frequent stirring.

Another official German publication, quoted in *Pharm. Zeit.*, 1907, p. 939, gives the following prescription for the preparation of Cresolic Soap (*Liquor Cresoli saponatus*): Heat 60 parts linseed oil on the water-bath in a roomy, loosely covered glass flask, and add, with agitation, a solution of 12 parts potassium hydroxide in 30 parts water and 6 parts spirit of wine. Continue the heating until the saponification is complete, and now add 100 parts of cresol, boiling-point 199° to 204°. The liquid thus formed should be clear and of yellow-brown colour.—It is pointed out that this prescription allows of preparing a cresol soap which is not merely of equal value as lysol in its general properties but even superior to it in disinfecting power.

Cresol Raschig (Ger. P. 87275; *Z. angew. Chem.*, 1896, p. 358) is intended to obviate the drawback of lysol and creoline, viz., rendering the skin and instruments greasy. Raschig agitates 200 parts cresol with 25 parts of 25 per cent. caustic-soda solution, and adds 100 parts olein and 25 water. This mixture is easily soluble in water, and is prepared in a few minutes.

Hirschsohn (*Fischer's Jahresber.*, 1893, p. 540) renders cresol soluble by mixing 100 parts with a solution of 50 rosin and 6 or 8 sodium hydrate in 12 to 16 water.

Hiscott (B. P. 20746, 1896) mixes 50 to 100 parts commercial carbolic acid with half its weight of melted rosin, sufficient concentrated caustic-soda solution, and 4 to 8 parts cotton-seed or cocoa-nut oil; or else ½ to 2 parts α-naphthol to 100 soluble phenol.

Raupenstrauch (Ger. Ps. 178794 and 178795) mixes the ordinary alkali-cresol soap with salts of heavy metals.

La Wall and Fullerton (*Amer. Journ. of Pharm.*, 1906, No. 4) recommend preparing *Liquor Cresoli saponatus* by means of freshly prepared potash soap.

Prescriptions for preparing cresol-soap solution by means of olein are given in *Pharm. Zeit.*, 1907, p. 500.

Jeyes (B. P. 16427, 1885) saponifies a mixture of carbolic acid with cocoa-nut oil by caustic soda, and makes the product more soluble by adding sodium sulphate or carbonate during the fusion. The product is sold by the name of *cylline.* Hargreaves (B. P. 18469, 1889) employs for this purpose the chlorinated phenols or their salts. MacArthur (B. P. 22332, of 1895) prescribes mixing at 200° F. 95·76 parts of 77 per cent. caustic potash with 250 carbolic acid or tar-oils, 255 oleic acid, and so much water that a liquid soap of 12 per cent. strength is formed; or else the oleic acid is first saponified and the disinfectant and water are added afterwards.

Cresolimentum, made by B. Hadra, is a 50 per cent. cresol-soap preparation.

Rosemann's "Carbolic-acid soap" (B. P. 28277, 1902) is made from water-white crude cresol, with 2 per cent. formaldehyde and 240 per cent. formaldehyde-potash soap (containing 15 per cent. COH). It is almost devoid of smell, easily soluble, not strongly poisonous, and very efficient.

According to a report made by the Royal Würtemberg Viticultural Institute on the work done in 1909, the solutions of cresol soap have done very good service for exterminating the shield-lice infesting the vines.

Carbolic-acid Soap is generally sold as containing 10 per cent. or even 20 per cent. of carbolic acid, but very often it contains much less (*cf.* Allen's analyses, p. 817), and in any case loses some of it in the course of time by evaporation. The cheaper descriptions contain mostly cresol; they can be made in the cold by kneading carbolic acid with curd soap and pressing into moulds, but preferably by melting the soap and mixing it with carbolic acid in the liquid state.

Many publications have been made in 1907 on cresolic soaps, which are reported on by Fortmann in *Chem. Zeit.*, 1907, p. 118.

II. *Soluble Carbolic-acid Preparations of Non-soapy Character.*

Helmers (Ger. Ps. 76133 and 80260) renders phenols soluble by means of the sulphonic acids of mineral or rosin oil.

The Chemische Fabriks-Aktien-Gesellschaft in Hamburg (Ger. P. 72101) found that the syrupy solution of the sodium or potassium sulphonates of phenylxylylethane and its higher homologues (remaining behind in the purification of crude xylol) dissolves tar-oils and cresols, without leaving the solution liable to be decomposed by acids.

Lembach and Schleicher (Ger. P. 73117) prepare soluble crystallizable, non-poisonous disinfectants, called *oxychinaseptol* or *diaphthern* by the action of 2 mols. ortho-oxyquinoline or its homologues on 1 mol. phenol or its homologues, 1 mol. sulphuric acid, and at least 3 mols. water. The new substance crystallizes in fine needles or large hexagonal prisms.

Ortho-oxyquinoline is also employed by Fritzsche (Ger. P. 88520). Two mols. of this substance are boiled ten or twelve hours in an alcoholic solution of 1 mol. sodium pyrosulphate till no further action takes place. The product, when cold, is separated from adhering alcohol, dried, and powdered. It is soluble in water, and the solutions dissolve phenols in every proportion; they are exempt from smell and irritating or poisonous properties, but strongly bactericidal. This *cresochin* contains 33 per cent. quinoline, and 17 per cent. cresols.

F. von Heyden's Nachfolger (Ger. P. 57842) make a solution of 12 parts sodium salicylate, 10 cold water, and 5 cresol, which can be diluted at will. Naphthol behaves in the same way. These preparations are sold as *solveol* for surgical purposes and *solutol* for ordinary disinfection; they are easily soluble, of constant composition, and do not render the hands, etc., slippery. Hammerl (*Chem. Ind.*, 1891, p. 298) declares a ½ per cent. solveol solution to be more effective against bacteria than 2 to 5 per cent. carbolic-acid solution.

Sozal (Scherges, *Pharm. Zeit.*, 1892, p. 489) is aluminium paraphenolsulphonate, crystalline, easily soluble in water, glycerin, and alcohol, and more efficacious than aluminium acetate in the treatment of ulcers, etc.

The *soziodols* of Trommsdorf unite the action of iodoform with that of carbolic acid in the treatment of wounds. One of these is more soluble, viz., the diiodparaphenolsulphonate of sodium, $C_6H_2I_2.OH.SO_3.Na$; another, the acid potassium salt, is less soluble.

Nördlinger's *saprol* (Ger. P. 70578), a dark-brown liquid, contains 40 per cent. cresol, 40 per cent. heavy tar-oils, and 20 per cent. petroleum hydrocarbons. It is not completely soluble, but floats on the sewage and gradually communicates to this its disinfectant property. It is well spoken of by Laser (*Centr. f. Bakteriol.*, 1892) and Scheurlen (*Arch. f. Hyg.*, 1893, p. 627), whilst according to Keller (*ibid.*, xviii., p. 57) the soapy disinfectants are preferable.

Phenosalyl is a mixture of carbolic acid, salicylic acid, lactic acid, menthol, glycerin, and borax.

Microsol is a solution of cupric sulphate, containing free sulphuric acid and 10 per cent. cupric phenolsulphonate.

Sanatolyse consists of carbolic acid, sulphuric acid, and ferrous sulphate.

Gentsch (Ger. P. 156761) first prepares solutions of phenols in benzol, chloroform, CS_2, etc.; by mixing them with dry alkaline carbonates, hydrates, or phenolates, crystallized double compounds of phenol and potassium phenolate are obtained, thus:

$$K_2CO_3 + 4C_6H_5.OH = C_6H_5OK.3C_6H_5.OH + KHCO_3.$$

The double compound can be separated from the alkaline bicarbonate by hot benzol or alcohol; after filtering from the $KHCO_3$ and cooling, the solution deposits shining needles of that compound, fusing at 106° to 108° C. The corresponding paracresol compound, $C_6H_4(CH_3)(OK).3C_6H_4(CH_3)(OH)$, fuses at 147° and is easily separated from the more soluble ortho- and meta-compounds by fractional solution. A second patent of the same inventor (Ger. P. 157616) prescribes working without solvents. He introduces, *e.g.*, solid caustic potash into para-cresol and heats until all is dissolved. On cooling, the whole solidified to a yellow crystalline mass of the double compound, as formulated above.

The Farbenfabriken vormals Bayer & Co. have obtained the B. P. 9953, 1904, for this process. The compound prepared by them is sold by the name of *Metakalin*, in the shape of tablets.

Kresulfol Riedel is a very cheap and efficient disinfecting mixture, made from 1 vol. crude cresol and ½ vol. commercial sulphuric acid. This mixture is applied in the shape of a 3 per cent. aqueous solution.

Busse (*Chem. Zeit.*, 1885, p. 602) employs phenol-zinc solution for preserving timber from dry rot and decay. The solution is laid on with a brush, preferably after being mixed with magnesia.

Albert Friedländer (Ger. P. 181288) makes phenol and the hydroxy-derivatives of complicated hydrocarbons soluble in water by the addition of comparatively small quantities of the sulphonic acids of benzene and toluene.

H. Schneider (Ger. P. 189960) prepares a dry mixture of anhydrous oxalic acid and cresol.

Schülke & Mayr sell the *o*-oxalic ester of phenol by the name *Phenostal.*

Kresosteril is prepared, according to the Ger. P. 229143 of the Rütgerswerke Aktien-Gesellschaft and C. Gentsch, by allowing a mixture of *m*-cresol and oxalic acid to stand in the cold, until the mass, which at first is semi-liquid, has solidified, and pressing it out very strongly. It decomposes already at 51°. Its disinfecting action has been studied by Bierotte (*Hyg. Rundschau*, 1910, xx., p. 1041, and 1911, xxi., p. 1).

Odourless antinonnin carbolineum is saponified ortho-dinitro-cresol-potassium.

A paper by Seel in *Z. angew. Chem.*, 1906, p. 271, treats generally of the part played by the numerous class of old and new cresol preparations.

Obermüller (*Berl. Ber.*, 1907, p. 3623) has studied in detail the action of sulphuric acid on phenols.

Carbolic-acid Powders, etc.

Several advantages are attached to disinfectants in a solid state. They are more easily handled, with less inconvenience to the outside world by leakages, etc.; there is also less danger of their being abused as poisons, whether accidentally or purposely, since they are not so easily swallowed as liquids. A number of the preparations mentioned before is already in the solid or pasty state; here we treat of those where the solid state has been purposely aimed at for this or that purpose.

Macdougal's Disinfecting Powder (*cf.* also p. 371) is a mixture of crude carbolic acid with impure calcium sulphite (made by passing sulphur dioxide over heated limestone).

Calvert's Carbolic-acid Powder is a mixture of carbolic acid with the siliceous residue from treating china-clay with sulphuric acid (in the manufacture of patent alum). It should contain from 12 to 15 per cent. of carbolic acid; but the percentage is often far below this; it is ascertained by distilling, say, 100 g. in a glass retort. The distillate is partly oily, partly aqueous. The oily portion should at least be tested with caustic-soda solution (p. 786), since it generally contains valueless indifferent tar-oils. The phenol contained in the aqueous portion can be estimated by bromine-water. Disinfectants containing lime should be slightly acidified before distillation.

Messrs C. Calvert & Co. have manufactured also a 50 per cent. preparation in tablets (*Chem. News*, xl., p. 38).

Süvern's Disinfecting Mass consists of lime, magnesium chloride, and tar, and only indirectly belongs to this class (Schroeder and Berens, *Dingl. polyt. J.*, cxxx., p. 134; *cf.* also *supra*, p. 371).

Ziurek (*Dingl. polyt. J.*, xxx., p. 134) prepares a disinfecting powder by slaking 100 parts of quicklime and adding 5 parts of carbolic acid, intimately mixing them. Köhler (*Z. angew. Chem.*, 1894, p. 515) has made an investigation of this "technical carbolate of lime." The brown colour required in the trade is obtained by adding the carbolic acid to the slaked lime while still quite hot, which favours the formation of rosolic acid. But this, as Köhler observed, may lead to the mass taking fire and burning out.

Heydenreich and Beilstein (*Fischer's Jahresber.*, 1881, p. 976) as well as Pettenkofer (*Cholera-Regulativ*, München, 1867) object to the application of caustic lime for the purpose in question.

Carbolic-acid tablets, for deodorizing the air in water-closets, hospitals, etc., are made by soaking pasteboard (Homburg, *Wagner's Jahresber*, 1880, p. 740; also Crace Calvert & Co., *cf.* above), gypsum (Reyhe & Söhne, Ger. P. 9094), or porous earthenware (Kubel, Ger. P. 9520) with carbolic acid.

Holtz's Phenolith (Ger. P. 6498) is made by dissolving anhydrous boric acid in phenol or cresol, which takes up about

40 per cent.; the mass forms a stiff paste, and can be converted into a powder by adding a little common salt, borax, or saltpetre. Lutze (B. P. 22136, 1897) mixes in a similar way carbolic acid with anhydrous boric or arsenious acid, alumina, magnesia, calcined borax, alum, or phosphates, to obtain non-hygroscopic powders.

R. Rütgers (Ger. Ps. 137584 and 141421) makes preparations of phenols with anhydrous oxalic acid.

Dowson (B. P. 11908, 1895) gelatinizes phenols by adding little beeswax, or carnauba-wax, paraffin, Chinese or palm-wax.

England (B. P. 16422, 1894) makes antiseptic manure by mixing antiseptic tar-products with superphosphates, if necessary with addition of gypsum.

Lysopast and *Phenopast* are mixtures of lysol and phenol of the consistence of a salve or paste.

Raetz (B. P. 27889, 1903) renders solutions of phenol- or cresol-soaps solid, to increase their action by treating them at high pressure with aldehydes or ketones.

Similar combinations are described in Speyer's Ger. P. 99570, in Henschke's Ger. P. 157533, in Stephan's Belg. P. 178849.

Investigations of the *poisonous action* of carbolic acid, the cresols, and cresol soaps have been made by Bokorny (*Chem. Zeit.*, 1906, p. 554); Jonescu (*Biochem. Zeit.*, 1906, i., p. 399; *Chem. Zentr.*, 1906, ii., p. 1510); Weil (*Chem. Zentr.*, 1907, ii., p. 2070); Wandel (*Zentr.*, 1907, i., p. 835; ii., p. 85); Bial (*ibid.*, ii., p. 85).

Condensation-products of Phenols with Formaldehyde.

In 1872 Baeyer showed that the phenols and aldehyde react upon one another (*Berl. Ber.*, v., 1095). At that time nobody thought of a technical application of this phenomenon. But when formaldehyde became a commercial product, obtainable at a moderate price, quite a number of inventors took up that reaction, and took out patents in that direction. So did Kleeberg (*Ann. Chem.*, 1891, cclxiii., p. 283); A. Smith (B. P. 16247, of 1899; Ger. P. 112685); A. Luft (Ger. P. 140552); Louis Blumer (B. P. 12880, of 1902); Fayolle (Fr. P. 335584);

Story (B. P. 8875, of 1905); De Laire (Fr. P. 361539); Baekeland (his numerous patents are described in *Chem. Zeit.*, 1909, Nos. 35 to 39, and 96); Leebach (Knoll & Co., B. P. 28009, of 1907; *Z. angew. Chem.*, 1909, p. 1589); T. Buser (Ger. P. 273192); Matsumoto (*Chem. News*, cxii., p. 195), etc.

The first class of these products, those prepared by Blumer and De Laire, is soluble in alcohol, acetone, and similar solvents, and in alkalis. They fuse on heating, do not harden when heated up further, and are known as "shellac-surrogates," because their physical properties are similar to those of shellac. The second class is principally represented by the products manufactured by L. H. Baekeland and Messrs Knoll & Co., and known by the designation *bakelite* and *resinite*, sold by the Bakelite-Gesellschaft in Berlin. These products are insoluble and infusible. They can be obtained directly from phenols and formaldehyde, but also (like bakelite and resinite) in two or more phases, the first of which is a soluble and fusible substance which only in the following phases is turned into the final state of an infusible and insoluble product. This allows of applying them in various ways, *e.g.* in the state of solution as varnishes, enamel, or for impregnating purposes, by casting or by pressing, with or without further condensation by heating under pressure into an insoluble and infusible state.

These products are very hard and resist nearly all chemicals; they are also very good insulators for heat and electricity. They can very well replace many natural and artificial substances, as amber, horn, bone, ivory, resin-lac, shellac, amber, vulcanized indiarubber, celluloid, glass, porcelain, etc., and, although they do not possess all their advantages, they are free from some of their drawbacks, *e.g.*, the easy inflammability of celluloid, the fragility of glass and porcelain, etc., etc.

We perceive that there is a wide field for the application of the products obtained mainly from phenol and the cresols. Baekeland has been studying the application of bakelite in upwards of forty various industries.

The Chemische Fabrik Dr K. Albert and Behrend (Fr. P. 471671) produce paint-oils and oils with increased antiseptic properties by forming resinous matters from phenols condensed with formaldehyde; or halogenated derivatives of the phenols may also be employed, and compounds of lead, copper, and mercury, and siccatives may be added, either before or after the condensation. The products may be used as paint-oils, especially for submarine purposes, and for impregnating wood.

Analysis of Carbolic-acid Preparations.

Two processes must be distinguished here: the estimation of phenol in the presence of soaps (creoline, lysol, carbolic soap), and the estimation of the efficiency of a disinfecting powder. All other cases can be treated by one of the previously described methods.

Allen (*Analyst*, 1886, p. 103) recommends the following process for *determining phenols in "carbolic soap"*:—Five g. weight of the sample are dissolved in warm water, with addition of from 20 to 30 c.c. of a 10 per cent. solution of caustic soda. The cooled solution is then agitated with ether, and the ethereal layer separated and evaporated at a low temperature. The weight of the residue gives the amount of hydrocarbons, etc. The alkaline liquid separated from the ether is then treated in a capacious separator with an excess of strong brine, which completely precipitates the fatty acids as sodium salts. The liquid is well agitated, and then passed through a filter. In cases where the soap does not readily coagulate, an addition of a small quantity of tallow or palm-oil soap, previously dissolved in water, will usually overcome the difficulty. The precipitated soap is washed twice with strong brine, the washings being filtered and added to the main solution, which is then diluted to 1 litre. One hundred c.c. of this solution (=0·5 g. of the sample of soap) are then placed in a globular separator, and acidulated with dilute sulphuric acid, when it should remain perfectly clear. Standard bromine-water is then added from a burette, the stopper of the burette inserted, and the contents of the burette shaken vigorously. More bromine-water is then added in the same way, until the liquid acquires a faint but permanent yellow tint. If crystallized carbolic acid has been employed for making the soap, the bromine derivative is precipitated in snow-white crystalline flakes, which allow the faintest yellow tint due to excess of bromine to be readily observed. If cresylic acid be the chief phenol present, as in the case of soaps made with Calvert's "No. 5 carbolic acid," the precipitate is milky, and does not separate well from the liquid, but the end of the reaction can still be observed. The addition of a solution containing a known amount of crystallized phenol is a useful device in many cases, as the precipitate then curdles readily, and the yellow coloration can be easily seen.

The bromine solution is made by mixing one measure of saturated bromine-water with two measures of water. This solution is approximately of 1 per cent. strength, and should be run out of a closely-covered Mohr's burette [no doubt a burette with glass tap would be preferable]. The last few cubic centimetres of the solution contained in the burette should never be employed. The bromine-water must be standardized immediately before or after use by a solution of Calvert's No. 2 or No. 5 carbolic acid, according to the kind of acid the titration has indicated to be present in the soap. This solution is made by dissolving 0·5 g. of the phenol in 20 c.c. of a 10 per cent. solution of caustic soda, together with 5 g. of a non-carbolic soap. The solution is then precipitated with brine in the same manner as the sample, the filtrate diluted to 1 litre, and 100 c.c. acidulated and titrated with the bromine solution used for the sample. The volume of bromine solution used is that required by 0·050 g. of coal-tar acid of approximately the same quality as that contained in the soap.

The remaining portion of the liquid filtered from the precipitate of soap is best used for isolating the bromo-derivatives. It is acidulated with dilute sulphuric acid, and bromine-water added in slight excess. From 5 to 10 c.c. of carbon disulphide is then added, the liquid well agitated, and the carbon disulphide tapped off into a small beaker. The aqueous liquid is agitated with fresh quantities of CS_2 (of 5 c.c. each), till it no longer acquires a red or yellow colour. The carbon disulphide is then allowed to evaporate spontaneously, whereby a residue is obtained, consisting of the brominated derivatives of the phenols present in the soap. If crystallized carbolic acid of fairly good quality had been used for preparing the soap, the bromo-derivative is obtained in fine long needles having very little colour; and if all heating has been avoided during the evaporation of the CS_2, the weight of the residue multiplied by 0·281 gives a fair approximation to the amount of carbolic acid. But if a crude liquid article has been employed, consisting mainly of cresol (cresylic acid), *e.g.*, Calvert's "No. 5 carbolic acid," the bromo-derivative will be deep yellow, orange, or red, with little or no tendency to crystallize, and the weight will not afford even a rough indication of the amount of coal-tar acid present.

By testing in this way, Allen found great deviations from the quantities of carbolic acid stated to be present by the manufacturers, *e.g.*, only 3·6 and 3·7 per cent. of phenol in "Carbolic Toilet Soap, ten per cent."

"Creolines" are analyzed by Weyl (*Berl. Ber.*, 1889, p. 138) as follows:—10 g. are extracted with 200 c.c. water, strongly acidulated with dilute sulphuric acid, well agitated, extracted with ether, and this extract is treated with caustic-soda solution. The alkaline solution is repeatedly treated with small quantities of ether, and the extracts are added to the principal portion. The total extract, containing all the *hydrocarbons*, is dehydrated by calcium chloride, filtered, cautiously freed from ether, left for twenty-four hours over sulphuric acid, and weighed. The alkaline solution is acidulated, treated with ether, and the ether treated with sodium-carbonate solution to extract the *acids*. The soda solution is acidulated with sulphuric acid and extracted with ether. The dehydrated ethereal extract is dried over sulphuric acid and weighed. The ethereal extract remaining after taking out the acids with sodium carbonate contains the *phenols*. It is dehydrated, cautiously evaporated, left twenty-four hours over sulphuric acid, and weighed. Soda is estimated by carbonizing about 3 g. in a platinum dish, evaporating with sulphuric acid, treating with ammonium carbonate, and igniting till the weight is constant.

We also mention the methods described by Beckurts & Otto (*Pharm. Zentralh.*, 1889, p. 227), Bodländer (*Reichs-Mediz. Anz.*, 1888, Nos. 10 and 11), Pfrenger (*Arch. Pharm.*, 1890, p. 701), Helbing & Passmore (*Pharm. Zentralh.*, 1892, p. 507), Engler & Dieckhoff (*Arch. Pharm.*, 1892, p. 507), Reuss (*Pharm. Zeit.*, 1894, No. 90), Spalteholz (*Chem. Zeit.*, 1898, p. 58), Fresenius & Makin (*Z. anal. Chem.*, 1896, p. 325).

An elaborate paper by Ditz & Clauser (*Chem. Zeit.*, 1898, p. 733) describes the separation of fatty acids and phenols, *e.g.* in lysol. They saponify the whole with 10 per cent. caustic-soda solution, extract the hydrocarbons from the solution with ether (afterwards evaporating the ether and drying over sulphuric acid), neutralize the remaining aqueous liquid with HCl, and add an excess of barium chloride, as well as sufficient barium hydrate solution for neutralizing the cresols. The barium oleate is thus precipitated in the cold; it is quickly filtered, washed first cold, then hot, rinsed into a beaker, decomposed by HCl, and the fatty acids weighed as usual. The cresols contained in the filtrate from the barium oleate might be extracted by ether and weighed; but more exact results are obtained as follows:—The filtrate is acidulated, brought to a known volume, and portions of this are titrated by Koppeschaar's bromine method (p. 799). Thus in the first instance the total bromine, a, is ascertained, which corresponds to all the phenols, which, however, absorb different quantities of bromine (p. 798). In order to ascertain the quantity of phenols, we must extract a certain portion of the acidulated solution by ether, evaporate the solvent, dry and weigh the residue $= g$. This phenol residue is now dissolved in caustic soda or baryta, and titrated by Koppeschaar's method; the bromine absorbed $= b$. If c is the original weight of lysol, the percentage of phenols is

$$\frac{100 \times a \times g}{b \times c}.$$

Spalteholz (*Chem. Zeit.*, 1909, p. 181) tests carbolic-acid soaps merely by an approximate estimation of their percentage of water, by means of titration with acetic acid until a permanent opacity is produced.

Disinfecting powders are more simply analyzed by distilling 100 g. (if containing lime, after adding sulphuric acid) in a glass retort and separating the oily and watery distillate. The former often contains a great deal of worthless tar-oils, and must be at least tested with caustic-soda solution (p. 786); the aqueous portion contains phenols, and must be tested by the bromine method.

Further papers on the examination of carbolic-acid disinfectants are by Williams (*J. Soc. Chem. Ind.*, 1888, p. 826), Muter & de Koninck (*Analyst*, 1887, p. 191), Staveley (*Chem. Zeit.*, 1889, p. 1126; extract, *J. Soc. Chem. Ind.*, 1889, p. 1012), and Swoboda (*Chem. Zeit.*, 1891, p. 1041). We can here only mention these; the originals must be referred to for full particulars.

A process worked out by Clessler consists in shaking 10 c.c. of the liquor in a graduated test-tube with 6 c.c. official hydrochloric acid and heating in the water-bath up to the complete separation of the oily layer.. After cooling down to 15°, the volume of the latter is read off. This process has met with several objections. Schmatolla (*Chem. Zentr.*, 1904, ii., p. 1518) describes a similar process. He puts into a 200 c.c. cylinder 50 c.c. dilute sulphuric acid, adds 100 g. (weighed) of the cresol-soap solution, shakes up, and allows to settle for an hour. At least 73 c.c. of cresolic oil should be separated, sp. gr. at 15° at least 1·004 after filtration, corresponding to 67 per cent. cresol in the oil, or 49 per cent. in the liquor. For each degree C. over 15° 0·0006 is to be deducted off the specific gravity.

A prescription (1904) of the German Board of Health for the testing of Liquor Cresoli saponatus is this: acidulate with sulphuric acid, distil by means of steam, shake the distillate with ether, evaporate the ethereal solution, and dry the cresols thus obtained. This prescription holds good also for testing any other preparations containing no neutral oils, such as lysol. The "drying" of the cresols, as pointed out by Russig, should not be performed by the application of anhydrous sodium or potassium carbonate, since these will take up some cresol, as proved by the compound found by Gentsch (p. 810) and by Russig in testing benzolic solutions of phenols.

The Society of Swiss Analytical Chemists (*Chem. Zeit.*, 1907, p. 1028) demands the following prescriptions to be fulfilled by cresol-preparations intended for disinfecting purposes, and as remedies against vegetable diseases. 1. They must be perfectly clear and soluble in water, alcohol, ether, petroleum, benzin, benzol, chloroform, and glycerin. 2. They must contain at least 50 per cent. phenols and cresols, boiling between 187° and 210°, as proved by distilling 100 c.c. in a 300 c.c. flask, in which the thermometer bulb goes down 10 mm. below the side tube, then adding a little common salt to the distillate, when there must be at least 45 c.c. of cresols separated out. 3. Cresol preparations for medical and veterinary purposes must have a neutral reaction against phenolphthalein, when shaken up with five times their bulk of salt solution and filtering off the solution.

Rapp (*Chem. Zentr.*, 1909, ii., p. 2207) mixes 20 c.c. cresolic soap (which must be quite free from alcohol) with 40 c.c. glycerin in a 200 c.c. fractionating-flask, distils half of it, not over 280°, into a graduated cylinder, mixes the distillate with the same volume of a mixture of 2 parts concentrated sulphuric acid and 1 part water, and reads off the volume of the anhydrous cresol. Into the flask, after cooling, he puts 100 c.c. hot water, pours the whole into a graduated cylinder, adds 20 c.c. or more normal sulphuric acid, then 10 c.c. petroleum spirit, and reads off the volume of the fatty acids separated. Or else he heats the soap solution with 2½ to 3 g. solid paraffin and 20 c.c. normal sulphuric acid on the water-bath, allows to cool, pours the liquid off from the solidified fat cake, washes this with 30 to 50 c.c. water, heats it on a small flame until all the water has evaporated, and weighs it—thus finding the percentage of fatty acids. The liquid poured off from the fat cake and the washings are united, and the alkali contents of the cresol soap is found by retitrating with normal alkali and phenolphthalein. The water contained in the sample is found by the difference. If the cresol is to be examined for neutral oils, it is separated from the acid by means of a tap-funnel, washed into a burette by 100 c.c. 9 per cent. NaOH solution, allowed to stand overnight and read off, if necessary after adding petroleum spirit. The fatty acids remaining in the flask after driving off the water are dissolved, with warming, in absolute alcohol, and titrated with NaOH solution and phenolphthalein. By deducting the alkali now found from that found at first, the excess of alkali in the cresolic soap is determined.

A simple process for the estimation of soap in tar-oil and cresolic soaps is described by M. Duyk (*Corps gras ind.*, 1908, No. 10). Twenty g. of the substance are put into a known quantity of hot water, and enough ordinary sugar is added to produce a clear syrup, which is heated, with frequent stirring, in a beaker on the water-bath, until the liquid has separated into two layers, an upper oily one and a lower watery one, which is transparent or a little muddy; this is separated from the oily layer by a tap-funnel and a concentrated solution of common salt added, whereby any soap present is quantitatively separated, filtered off, washed with salt solution, dried, dissolved in strong alcohol, and separated from it in a pure state.

Applications of Carbolic Acid and of the Cresols.

Several such applications have been already mentioned in the preceding pages.

Application for Medical and Antiseptic Purposes.—Carbolic acid is widely used for antiseptic purposes, but mostly in the crude state. For *disinfecting* sewers, stables (in the case of cattle-diseases), or even human dwellings, the cheaper descriptions, which are liquid and contain cresol, are probably as valuable as crystallized phenol, and also for preserving hides, bones, etc., for sea transit. The *preservation of wood* by pickling with creosote oil is founded, at least partially, on the same principle. The *preservation of meat* in the same way has often been proposed, but does not appear to be practicable, owing to the very tenaciously retained smell and taste of carbolic acid. *Beetroot juice* can be preserved by it, as shown by Cunisset (*Bull. Soc. Chim.*, 1874, xxi., p. 47) and Hulwa (*Wagner's Jahresber.*, 1875, p. 795). Maercker (*ibid.*, 1872, p. 826) recommends it for destroying the lactic-acid ferment in the manufacture of alcohol.

Kellner (*Chem. Zeit.*, 1884, p. 122) found that carbolic acid is a good remedy for the *parasitic diseases* of plants and animals; manure containing 2 per cent. of it is harmless to the plants, except when put on the field together with the seed.

Carbolic acid is very important for *preserving skins;* Kletzinsky (*Wagner's Jahresber.*, 1864, p. 601) showed that it possesses *tanning* properties; and Baudet (*ibid.*, 1870, p. 669) obtained a patent for this purpose.

Harcke (Ger. Ps. 16022 and 19633) adds carbolic acid in the currying process to the usual mixture of alum and salt; he also makes "artificial leather" by treating fabrics first with a solution of glue and then with a mixed solution of alum, salt, and carbolic acid. Shaw (Ger P. 27270) and Beda (B. P. 16647, 1886) proceed in the same manner.

Crude sodium carbolate is employed as a protection against *dry-rot*, under the name of "house preservatory."

For medical purposes, especially for internal use, as well as for Lister's antiseptic treatment of wounds, and for cleaning the instruments, hands, and clothes, the purest crystallized acid is always preferred, both on account of its higher solubility and its less unpleasant smell, which can be entirely masked by a little oil of geranium.

It has been noticed in the application of the phenols for *surgical* purposes that the cresols are preferable in this application to carbolic acid; they seem to have even superior antiseptic properties, whilst acting less irritant to the skin. Hence there is not much phenol used in that way.

Applications of Carbolic acid and of the Cresols for Technical Purposes.—In the pure state phenol is employed in the manufacture of artificial colours, especially of *picric* acid and *corallin*; these are not very much used as colours now, but picric acid and its salts are extensively utilized in the manufacture of *explosives*, such as "melinite" and "lyddite," and probably the greater part of the carbolic acid produced at present finds its way into the explosives factories. Also some azo-colours have been made with it; and undoubtedly many other applications of it and its homologues will follow in this direction. But it is very doubtful whether it will ever pay to employ phenol as a starting-point for preparing rosaniline, as has been proposed. Phenol is also the starting-point for the manufacture of *salicylic* acid, and a good deal is used for this purpose.

The Neue Augsburger Kattunfabrik (Ger. P. 95692) employs a weak solution of phenol (1 : 4000 water) in calico-printing for removing the gum.

Gassmann and the Usines du Rhône (Ger. P. 99756) employ phenol and cresols for dissolving colouring-matters insoluble in water.

Justin Mueller (*Bull. Soc. Ind. Mulhouse*, lxxvi., p. 72) finds that an addition of phenol to the colours for printing on wool has the same effect as chlorinating the wool.

The Badische Anilin- und Sodafabrik (Ger. P. 158500) purify indigo by heating it with three times its weight of phenol to 120° to 140°, whereby a product of nearly 100 per cent. indigotine is obtained.

Bühler (Ger. P. 94467) has found that the phenols and tar-oils containing them, when heating them under pressure with wood, dissolve the lignine and leave the cellulose in a pure state. For 1 part of wood he heats 4 parts of phenols or tar-oils containing 50 to 60 per cent. phenols to 180° for three to five hours under pressure. The mass obtained, when pressed out, still contains from 25 to 30 per cent. oil which must be removed by appropriate solvents.

Casselmann (Ger. P. 116913) regenerates indiarubber from waste rubber of all kinds by heating for some time with carbolic acid to 120° to 170°, whereby the sulphur is split off and the pure rubber is dissolved. When extracting the carbolic acid by aqueous or alcoholic solutions of alkali, a very elastic product is obtained, free from the unpleasant smell of ordinary rubber. *Cf.* also the Ger. P. 154911 of Chantard and Kessler.

The Bakelite Ges. m. b. H. (Ger. P. 281454) prepare condensation products from phenols and formaldehyde in the presence of bases serving as condensing-medium, for the manufacture of varnishes.

The Hüssener Gewerkschaft (*Z. angew. Chem.*, 1889, p. 132) manufacture basic lining stones for converters by melting powdered chrome iron-ore, limestone, dolomite, and magnesia with sodium phenolate, free from oils.

Statistics.

Reliable statements on *the total production of phenol and cresols* we can quote only from Germany. According to the data published by the Imperial Home Office in the *Nachrichten für Handel und Industrie*, 1910, No. 31, there was produced in the year 1908 in German tar-works 1000 tons crystallized carbolic acid, 2081 tons cresols (so-called 90, 95, and 100 per cent. carbolic acid), and 581 tons crude phenols for sale. In the same year, as stated by Raschig, there was produced in the *pure* state about 100 tons *o*-cresol, 200 tons *m*-cresol, and 50 tons *p*-cresol.

The *importation of phenol* (crude and purified) into Germany ranged from 5106 tons, in 1903, to 4239 tons in 1910; the exportation from 3102 tons to 3998 tons. Of *cresol* there was imported in 1906, 9·8 tons; in 1910, 120 tons; exported in 1906, 316 tons; in 1910, 721 tons.

NAPHTHALENE.

Naphthalene is always contained in coal-gas, and as it gives rise to troublesome crystallizations in the gas-pipes, a number of processes has been devised for taking it out of the gas; but this does not belong to our present task, no more than the recovery of naphthalene from natural mineral oils.

Crude Naphthalene.

Naphthalene is one of the most abundant constituents of coal-tar. Its proportion is rarely below 5 per cent., and it may amount to perhaps 10 per cent. of the weight of the tar. Large quantities of it are obtained in the crude state, by the cooling down of creosote and middle oil as described *supra*, pp. 650 and 729; the first portions of this sometimes solidify almost entirely. This crude naphthalene was formerly considered a nuisance, as the buyers of creosote oil objected to it, and there was no outlet for it. Even now sometimes part of the naphthalene contained in coal-tar must be utilized as an admixture to creosote oil or as fuel; but there is already a considerable demand for it in the industry of artificial colours (for the preparation of naphthols, naphthylamine, and its sulphonic acids, phthalic acid, and especially for the synthesis of indigo), also for carburetting gas, and recently as fuel for explosion-motors (*vide infra*).

It is very natural under these circumstances that sometimes the naphthalene obtained by the cooling-down of creosote oil is not sufficient for supplying all that is demanded in the trade, and that proposals have been made for increasing the yield of it.

According to Tammann (Ger. P. 95579), naphthalene and its homologues can be recovered from the acid-tar of refining petroleum. This process can hardly be advantageously employed for naphthalene itself, but may do perhaps for the di- and trimethyl-naphthalenes.

Livesey and Kidd (Amer. P. 258778) propose preparing naphthalene by heating "dead oil" in a closed boiler, and passing a current of air over the surface of the liquid. The air carries off the naphthalene and a little oil, which are condensed in a chamber. The condensed mass is immediately utilized for the manufacture of an article suitable for carburetting air or gas, by reheating it and casting it in cold-water jacketed moulds, like candle-moulds, but wider at the top. The sticks are taken out of the moulds the moment they are set, and the oil (which floats on the surface) is wiped off before it can sink into the naphthalene. The oil would not separate without the water-jacket. This process can at the best only yield a partially purified sort of naphthalene. In Europe, at any rate, only such naphthalene is now saleable which does not readily turn pink on exposure to the air; and this can only be made by more careful treatment, including hot-pressing, chemical washing and distilling.

Mallmann (Ger. P. appl. M25601, of 1906) also proposes obtaining naphthalene directly from tar or tar-oil by means of a current of air.

M. Mayer (*J. Soc. Chem. Ind.*, 1915, p. 166) recovers naphthalene from pastes for the manufacture of briquettes (patent fuel) by drying in a current of air at 40° to 60°.

Strommenger (*Z. angew. Chem.*, 1915, ii., 371) describes a naphthalene washer for coke-oven gases.

Purification of the Crude Naphthalene.

The crude naphthalene, as it comes out of the draining-boxes of the cooling-house, contains still from 10 to 15 per cent. of the oil from which it has crystallized. This oil depresses the solidifying-point of the naphthalene (which in the *pure* state of this hydrocarbon is 79°·6 to 79°·8) to 58° to 60°, and imparts to it a certain percentage of acid oils and bases. This adhering oil must therefore be removed, if the naphthalene is required in a pure state. The following description is principally based on the statements of Rispler (*loc. cit.*).

A large English factory formerly omitted this, and submitted the naphthalene coming out of the draining-boxes at once to a first distillation, in which the first 10 per cent. were taken as crude "first runnings" and the next 70 per cent. run into open casks; the remaining 20 per cent. went into the dead oil. The casks were left standing in a cool place for a week; then the inner, oily portion was taken out and the outer portion, now nearly free from oil, was left lying on an inclined place for a week, to be drained, whereupon it went to the chemical treatment (*vide infra*). But this very primitive proceeding is probably not in use anywhere now.

The first operation is in any case the removal of the adhering oils in a mechanical way, which was formerly effected by *cold hydraulic presses*, or by *centrifugals.* The latter get out much more of the oil, but still leave a few per cent. of it in the naphthalene which cannot be removed by the subsequent treatment with sulphuric acid and caustic-soda solution. Part of this oil can be got out by steaming in the centrifugals. The only rational proceeding is: hydraulic pressing with application of *heat.*

The *hot-pressing* of the crude naphthalene is carried out in various ways. The apparatus formerly used was a *horizontal* press, containing from 40 to 60 perpendicular hollow plates, heated by steam. Between the plates the naphthalene is placed in camel-hair cloth. The steam is carried to the plates in two pipes of different width, one inside the other, with a stuffing-box at the junction. An iron box below the plates receives the oil pressed out, which is put back into the cooling-boxes. The preparation of the cakes for the press is made in two different ways. The first of these consists in placing the drained crude naphthalene in jute cloths, pressing it first in perpendicular cold presses and then putting it, with the cloths, into the hot press. The second way is this: casting the drained crude naphthalene in box, provided with a heating-coil, and pouring it into shallow moulds, a little smaller than the plates of the hot press. After cooling, the cakes are taken out of the moulds, placed in the cloths belonging to the hot press, and the press is started, applying heat to it. The edges of the pressed cakes, which are not exposed to the pressure, and still contain much oil, must be cut away after taking the cakes out.

The process described here yields a very good quality of pressed naphthalene, but it is very troublesome, lengthy, and expensive through the great waste of pressing-cloths and the loss of heat connected with the open construction of the press. A very important improvement, therefore, was the introduction of *perpendicular hydraulic hot presses*, which did away with the necessity of casting cakes or preliminary pressing, as well as with the waste of pressing-cloths. Such a press is supplied by Messrs Brinck & Hübner, of Mannheim, by the name of "Ring-Press." It consists of a large number of iron rings with movable perforated bottoms, suspended between perpendicular columns, and heatable by steam conducted to them and away from them by flexible metallic tubes, which are connected with a common inlet and outlet-pipe. Every ring has in its circumference a channel in which the pressed-out liquid collects, and runs off at the bottom. The naphthalene coming from the draining-boxes is by special machinery converted into a uniform paste, and in this state introduced into the press-rings. One set of these rings is always under pressure, while another set is getting emptied and re-filled. Each operation, including filling and emptying, lasts half an hour and furnishes about 2 cwt. of pressed naphthalene, which is at once ready for further treatment. The pressure goes up to 300 atmospheres, that is twice the pressure attained in the horizontal presses.

In very large factories another style of perpendicular presses is employed which go by the designation "Sifting-presses" (in German: "Seiherpressen"), and consist of heatable steel cylinders, provided with a great many fine openings. There are several forms of this style of presses; two of these are especially recommended, viz., those sold by the aforementioned firm, Brinck & Hübner, of Mannheim, and those sold by Koeber's Eisenwerk, of Harburg-Hamburg. These firms will supply all necessary information to intending purchasers.

Other Methods for Removing the Oils from Crude Naphthalene.—Rispler (*loc. cit.*, No. 82) mentions a process, worked out by him in 1896, at a time when the new constructions of presses had not yet been worked out to their present state of perfection and economical function. The oils contained in crude naphthalene were to be converted into soaps, similar to creolin, sapocarbol, etc. (*vide supra*, p. 807), and by washing these out by means of water, naphthalene free from oils was to be obtained. This process could only pay, if the waste liquor could be utilized for the preparation of tar-emulsions, such as they were employing at that time for impregnating railway sleepers, and it does not appear to have been carried out in actual practice.

Paradill-Mateu (B. P. 25989, of 1903) causes a current of air or other gases to act upon the naphthalene vapour in the subliming-chamber, or upon the distillate coming out of the stills, which should be kept at 79°. The naphthalene is condensed here, while the less easily condensing vapours are carried away by the gaseous current.

Chemical Purification of the Pressed Naphthalene.—The naphthalene, as it comes from the hot presses, is nearly pure; it has already a solidifying-point nearly approaching that of pure naphthalene (79°·8); but it still contains a little foreign matter, as proved by its not being perfectly white. For many purposes it can be used in that state, but where it is required to be absolutely pure, it must be submitted to a chemical washing with concentrated sulphuric acid and caustic-soda solution.

In some places (and formerly this was the usual manner of proceeding) the chemical treatment begins with washing by means of *caustic-soda solution*, of any convenient strength. This is effected in closed iron vessels, heated above the fusing-point of naphthalene by a steam-jacket or a coil, and preferably provided with a mechanical agitator. With very impure naphthalene this treatment should be repeated. In any case the fused naphthalene must be mixed up for some time with the liquor, and after the latter (which collects at the bottom) has been run off, the naphthalene should be washed with hot water, which will now rise to the top.

In the case of better crude naphthalene, especially that distilled from carbolic-oil residues, the alkaline treatment may be dispensed with, and the washing begun with *sulphuric acid*, which in the concentrated state removes the residual phenols in the shape of sulphonic acids. Vohl (*J. prakt. Chem.*, cii. p. 29) recommends sulphuric acid of 45° Baumé (=sp. gr. 1·453). According to my experience this is too weak; acid of at least 1·740 sp. gr. should be employed. The strongest acid, of sp. gr. 1·84, is even better; but at that temperature it dissolves much naphthalene, so that less, though of a better kind, is obtained. At some works they wash first with dilute and then with strong sulphuric acid. On the large scale about 5 per cent. of acid will suffice; sometimes 3 per cent. is sufficient.

The mixture with sulphuric acid is effected in wooden or iron vessels lined with lead, or best of all in cast-iron cylinders.

heated by indirect steam and provided with an agitator, as they are described in the next chapter for the chemical treatment of crude benzol. The sublimation of naphthalene during this operation is rather troublesome. Now follows washing several times with water and then with weak alkaline liquor, to remove all acid, and finally distillation (see below).

Rispler (*loc. cit.*) points out that the action of the ordinary agitating-apparatus is very slow, because the sulphuric acid is not lifted high enough, and does not reach the upper layers of the liquid to be washed. In order to remedy this drawback, he has aided the action of the mechanical agitator by a current of compressed air, introduced below the sulphuric acid at the bottom of the vessel. But this is objectionable, since the air will carry away a sensible quantity of naphthalene vapour. Rispler has also taken out a German patent (No. 86502) for a washing-apparatus, which can be used both for naphthalene and for crude benzol, which is supposed to be more efficient than the ordinary apparatus described in the next chapter.

To begin with, Rispler treats the naphthalene with 5 per cent. sulphuric acid, which has already served for washing naphthalene, for twenty minutes, in order to remove any moisture present, as well as the pyridine bases. After allowing some time for settling, the acid is drawn off, and 5 or 6 per cent. fresh pure acid of 60° Baumé is added and agitated with the fused naphthalene for half to one hour. After drawing off this acid (which serves the next time for the first washing) follows a washing with hot water (say, 4 per cent.), and after this a treatment with once-used caustic-soda solution of about 20° Bé.; ultimately a washing with 2 per cent. hot water—no more, because otherwise the separation of the liquids, when at rest, is imperfect. The washed, still liquid, naphthalene can go to the stills; but Rispler recommends putting it first into an inclined vessel, allowing it to rest for some time, and drawing off the last portions of water collecting after some time. The amount of sulphuric acid of 60° Bé. used in this process is 5·7 per cent., that of caustic soda 0·47 per cent., the loss by washing 4·3 per cent., all of this referring to 100 parts of pressed naphthalene. The purified naphthalene obtained on the large scale showed a solidifying-point of 79°·7, and 97·5 per cent. of it distilled within the limits of 216°·6 to 218°. The final results of the purifying process, for 100 parts of pressed naphthalene, are (according to Rispler): pure naphthalene 89·13 per cent., residue 4·87 per cent., loss by washing 4·30 per cent., loss by distillation 1·70 per cent.

Treatment for Preventing the Reddening of Naphthalene on Keeping.—Before distillation, some manufacturers employ an oxidizing treatment in order to avoid a subsequent reddening of the naphthalene. (Dr Kraemer informs me that he considers this treatment as superfluous.) At an English works they add to the melted naphthalene 1 per cent. potassium bichromate and the necessary quantity of sulphuric acid, sp. gr. 1·7, agitate for two hours, add a little water, agitate another half-hour, allow to settle for two hours, and draw off the green liquid at the bottom. Following this comes the washing with sulphuric acid, sp. gr. 1·84, then with dilute water, and at last with pure water to which enough sulphate of soda is added to render the specific gravity sensibly greater than that of the fused naphthalene.

I have (*Berl. Ber.*, 1881, p. 1755; *Chem. News*, xliv., pp. 65 and 142) succeeded in thoroughly purifying naphthalene by treating it with a few per cent. of "Weldon mud" (recovered manganese dioxide, or rather calcium manganate) and sulphuric acid of sp. gr. 1·7 or 1·84. Even ordinary ground manganese ore can be employed for this purpose, by mixing 5 per cent. of it with melted naphthalene, adding 10 per cent. sulphuric acid, gradually or in two portions, and stirring for half an hour or an hour.

Naphthalene from washed carbolic oil requires no alkaline treatment. At the present low prices of naphthalene most manufacturers employ only sulphuric acid and very little caustic-soda solution.

Special Processes for Purifying Crude Naphthalene.—G. Link (Ger. P. 35168) presses crude naphthalene repeatedly in hydraulic presses, distils it, and treats the distillate, in a cast-iron agitator, similar to those used for manufacturing nitrobenzol, with a solution of soap at about 85°. Most of the mass enters into solution; the mixture is run into wooden tanks, is cooled down to 50° by cold water, dehydrated in a centrifugal machine, washed and distilled. The naphthalene now passes over almost chemically pure, as a limpid liquid, which solidifies to a large-flaked, snowy-white, crystalline mass. The impurities of crude naphthalene remain dissolved in the mother-liquor.

Dehnst (Ger. P. 47364) treats naphthalene with ½ or 1 per cent. brimstone at 170° or 175°. The impurities he states are changed thereby into high-boiling substances, whilst the naphthalene is not affected.

Stenhouse and Grove (*Berl. Ber.*, 1876, p. 683) heat the otherwise purified naphthalene with a small percentage of sulphuric acid to a temperature of 180°, distil the resulting black mass in a current of steam, and repeat this process till the product dissolves at 100° in an excess of concentrated sulphuric acid without any colour. This process, employed by them for scientific purposes, would hardly pay on the large scale, and it would be very troublesome to sublime the naphthalene mixed with acid.

From Dr H. Köhler I have received the following communication on the manner in which he prepares technically pure naphthalene for the manufacture of naphthol and naphthylamine. The crude naphthalene, as it is obtained from creosote oil, etc., is allowed to drain on a plate with fluted surface, having been reduced to pieces of the size of a walnut or a hen's egg, in a layer of from 4 to 5 ft. deep. After this draining it is submitted to cold hydraulic pressure at 200 atmospheres, and is then distilled in the still for crude naphthalene, described *infra*. The distillate up to about 210° C. is received as "first runnings," and kept separate from the main distillate, coming over between 210° and 228°. The latter is run into a receiver, heated by a steam-coil, and from this into shallow cast-iron moulds, where it very quickly forms cakes about 2 in. thick. These are wrapped in sheets made of coarse hemp cloth and placed in frames which give them an exact shape. The parcels thus formed are placed between perforated iron plates and built up with these in the hot press, where a wrought-iron grid is placed between each parcel and the heating-plates, so that the oil produced on pressing can run away. When the press is full, its temperature is raised to 70° or 75° by means of steam, and the pump is started. The pressure is *slowly* raised to 200 atmospheres; this pressure is maintained for some time, until no more oil runs off. Usually one pressing is sufficient; but some descriptions of naphthalene require a second pressing, as manifested by the oily appearance of the margins of the cakes. In this case the cakes are broken up, repacked as above described, and pressed over again.

Now comes the chemical treatment. The pressed naphthalene is melted in an apparatus provided with a mechanical stirrer, and is treated with sulphuric acid at a temperature not exceeding 100° C.; employing first about 2·5 per cent. of its weight of acid of sp. gr. 1·84, for the purpose of dehydration, and thereupon 5 to 7·5 per cent. by weight of acid, sp. gr. 1·70, the quantity varying according to the quality of the crude naphthalene. After running off the acid, or, preferably, forcing the naphthalene through a heated pipe into a second washing-apparatus, it is repeatedly washed with hot water, as described above.

The purified naphthalene, while still liquid, is forced into a still; here it is mixed with 5 per cent. of its weight of caustic-soda solution, sp. gr. 1·38, and after being separated from the salts is distilled as described lower down, observing the thermometer and taking samples from time to time. The first runnings of both distillations are worked up as previously described. The last runnings from the second distillation may be worked up for naphthalene in bars or balls.

Distillation of Naphthalene.

The stills are sometimes shallow wrought-iron vessels, holding a ton or upwards, heated by a direct fire, but protected against its first action by a curtain-arch; they are provided with a manhole, a safety-valve, and a very high head (up to 7 ft.), which can be furnished with contrivances for dephlegmation, but which already acts in this direction by the cooling effect of the air.

Sometimes larger stills are employed, holding from 10 to 20 tons of naphthalene, with dephlegmating-columns 6 to 10 ft. high, as they have been described *supra*, p. 752, for the distillation of middle oils. The distillation of naphthalene goes on very easily and quickly, but proper arrangements must be made for avoiding trouble by the solidification of naphthalene in wrong places.

The condensation is effected by a simple iron worm similar to those used for tar, but the water in the tub is always kept at least at 80° (for which purpose a steam-pipe must be provided for the cooling-tub); sharp elbows and the like (where at the end of the operation solid naphthalene might accumulate and cause in the next operation a dangerous tension in the still, or ultimately an explosion) should be avoided. If after all a plug of naphthalene should choke up the worm without its presence being at once detected (in which case it could be melted by boiling water), the safety-valve will blow out. This is a signal for instantly drawing out the fire; in the worst case the still must be cooled from above by pouring water upon it.

All danger of choking up is avoided, when distilling in a vacuum, by employing an air-tight receiver and exhausting the air by means of a pump; and we would greatly recommend this method of distilling naphthalene for other reasons as well.

In lieu of an ordinary safety-valve (which easily gets fixed, and anyhow might not act quickly enough) a contrivance like that shown in Fig. 173 is sometimes employed. Upon the still is fixed a flanged pipe, *a*, 12 in. wide, covered by a metal plate, *b*. Hemp packing and the weight of *b* suffice for keeping the joint tight without screwing down the arm *c*. The latter is quite loose, and its only object is to prevent the cover *b* from being violently jerked away whenever it is lifted by excessive tension in the still; the cover will then be lifted as far as *c* allows it, and will permit the vapours to escape.

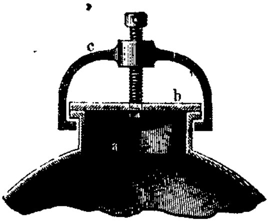

FIG. 173.

Watson Smith (*J. Soc. Chem. Ind.*, 1882, p. 343) thinks it safer and simpler to have a small hole bored in the still-top and closed by a cork, which, if there is too much pressure, would be blown out with some force. For large stills the outlet thus gained for the vapours would be hardly sufficient. Compare also what has been said respecting tar-stills, pp. 416 and 448.

Some manufacturers, in order to avoid any danger of choking-up, work without a worm, with an apparatus similar to that shown in Fig. 174. The vapours pass through the tube *a*, kept warm by the steam-pipe *b b*, into the wrought-iron cylinder *d*. Opposite *a*, running in the same slanting direction, is a pipe *c*, through which the steam-pipe *b* comes out. Thus *a* is prevented from being choked up, and *c* also serves for an occasional cleaning-out. The cylinder *d* is placed up to two-thirds of its height in a wider cylinder, *f*. If the cooling effected by the outer air is not sufficient, water is run upon *d*, which collects in the outer cylinder and runs away. But the temperature in *d* is kept high enough for the naphthalene to remain liquid and to run out through the pipe *e*. It is collected in shallow iron dishes, where it solidifies into cakes, which are either broken up and packed at once, or again subjected to hydraulic pressure.

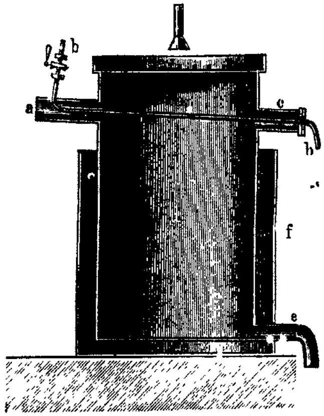

Fig. 174.

In distilling, first of all a little water and light oil appears. When the thermometer (in the vapour) has risen to 210°, the receiver is changed and pure naphthalene collected up to about 230°. Then either the still is stopped and the residue run to the creosote oil, or the distillation is continued into another receiver, and the impure naphthalene collecting there is again purified. Apart from the danger of choking-up, the distillation is easy and quick.

When redistilling the washed naphthalene, there is a small quantity of aqueous first runnings. After this follow 80 per cent. of pure naphthalene, which can be directly run into casks lined with sized paper and allowed to solidify. The distillation is continued so long as a sample, solidified on a watch-glass and covered with pure sulphuric acid (1·84), does not stain this yellow and dissolves therein on heating with at most a faint brown colour. As the by-products are always worked up again, the yield of pure naphthalene is about 70 per cent.

Distilled pure naphthalene is mostly employed for the manufacture of naphthols, naphthylamine, phthalic acid, etc. For medical purposes and as an insecticide (against moths, etc.), it is preferable used in the shape of scales or powder. This can be produced either by recrystallizing pure distilled naphthalene or by sublimation (see below).

Recrystallization of Naphthalene.

This operation is nowadays but rarely carried out, only in such cases where the naphthalene is required in dense, foliated crusts for special purposes, mostly for preparing certain substances in a pure form. The solvent employed is usually petroleum spirit. It is done in enamelled iron vessels provided with reflux cooler, and heated by steam. The solution is either allowed to cool directly in these vessels, or else in other vessels provided at the bottom with a tap for drawing off the mother-liquor. The crystals are centrifugalled and dried in the air. The coarser the crystals, the more are they favoured in trade; they are also more easily freed from solvent.

At some places amylic alcohol is used for recrystallizing naphthalene, in which case hardly any solvent is lost by volatilization.

Moulding of Naphthalene into Sticks, Globes, Powder, etc.

The distilled naphthalene is always run out of the condenser in a liquid form, and is usually run upon a large metal plate or shallow pan, where it solidifies, and is then broken up into small pieces, and sometimes ground into powder which is sent out in bags holding 2 cwt. each. Special smaller moulds are occasionally employed. The naphthalene required for the albo-carbon light (see below) is cast into sticks, like those of refined sulphur ("brimstone in rolls"). This is done by means of hardwood moulds, with a little taper to facilitate the getting out, or by a moulding-machine such as is used at candle-works. A special machine for this purpose is that of Neujean (Ger. P. 36708).

The conversion of pure naphthalene into powder is effected by the Rütgerswerke-Aktien-Gesellschaft (Ger. P. appl. R28802 of 1910) by blowing fused naphthalene at a temperature not much above its fusing-point by means of air compressed to 3 to 6 atmospheres through tuyeres into a chamber, the temperature of which is kept at about 30°, where the naphthalene collects in the shape of fine dust or coarser powder, the size of which is regulated by the amount of air-pressure and the tuyeres, and which is quite uniform.

Where large quantities of pure naphthalene are made, the *vapours* arising from the liquid naphthalene in the moulds, previous to its solidification, may cause an appreciable nuisance. This is prevented by providing the pan, serving as a mould, with a hydraulic lute, and fitting it with a cover suspended from a crane, so that it can be removed after the naphthalene has cooled down, in order to clear the mould. This apparatus resembles the oxide-of-iron purifiers of gas-works.

Naphthalene in the Shape of Rods (*like Candles*) *or Globes* is required for various purposes, such as the disinfection of the basins in public water-closets, for the destruction of moths, etc., and is manufactured in considerable quantities. Formerly this was done by casting the naphthalene in the well-known, complicated and expensive moulds made of bronze or tin. Nowadays the naphthalene rods are still cast in moulds like those used for the manufacture of stearine or paraffin candles. The globes, however, are always made in presses, containing a matrix with six holes and twelve dies, with semi-globular holes. Six of these are movable in the matrix; the other six are fixed on two eccentric rings. Ground naphthalene is continuously supplied to the holes by a funnel; the upper dies on going down mould it into globes, which are pushed out by the lower dies. The press, with 55 revolutions of the driving pulley, turns out 15 sets of 6 globes each per minute, that is 90 globes, weighing 3·5 g. each, or in ten hours' day-work 54,000 globes. One man can attend to one mill and two presses. They are sold by Dühring's Patentmaschinen-Gesellschaft in Berlin.

Sublimation of Naphthalene.

The subliming of naphthalene does not require a distilled article to start with; it suffices to employ the naphthalene after treating it with sulphuric acid and alkali, or the second quality of the distilled product. The subliming can be done on a moderate scale in the apparatus, Fig. 175 (taken from Wurtz).

a is a pan for melting the naphthalene, heated by the fire on the grate *b*; *c* is the snore-hole; *d d* are flues. The pan is covered by a tub, *f*, suspended by chains from a small crane, *e*; in its top there is a small air-vent. The naphthalene sublimes into the tub, forms crusts on the sides, and is knocked out at the end, after moving the tub sideways. The fire should not be strong enough to cause the naphthalene to melt in the tub and run back into the pan.

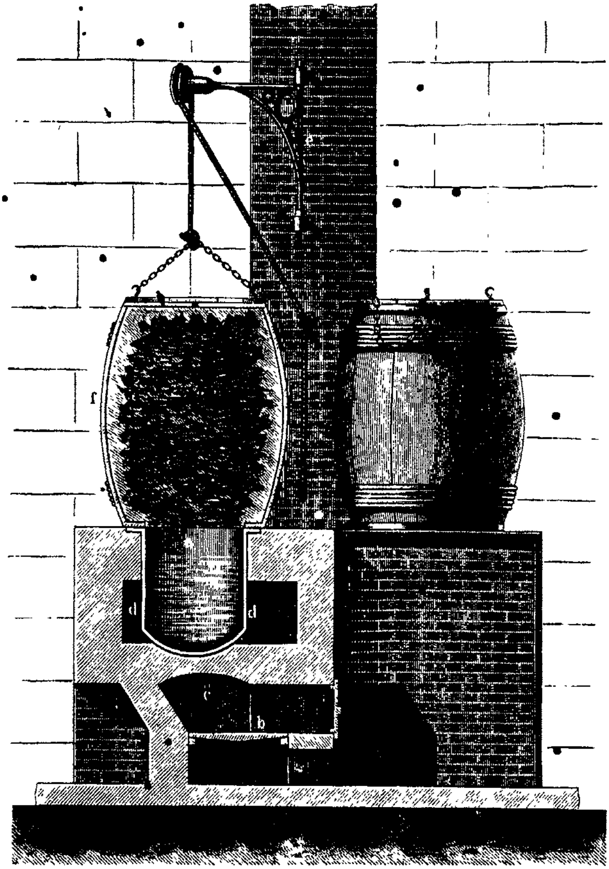

Fig. 175.

The apparatus, Fig. 176, is intended for a larger scale of working. *a* is a shallow iron pan, say 10 ft. × 7 ft. × 3 ft. deep. The steam-coil *b* on its bottom serves for heating. The pan is covered by the slanting wooden roof *c*, whose lower part can be turned back into the position shown by the dotted lines. To this is attached a wooden chamber, *d*, say 16 × 10 × 5 ft., with a working door, *e*, and a flap on the top, serving as safety-valve. The heat of the "dry" steam in the coil *b* suffices for subliming the naphthalene; it should not go so far as to give rise to distillation. The naphthalene collecting in *d* is taken out at intervals of a few days.

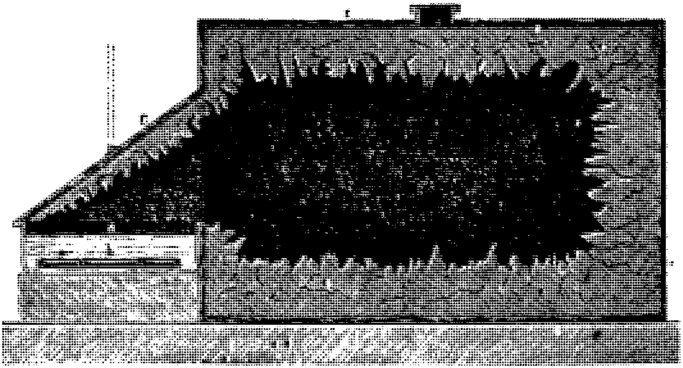

FIG. 176.

Sometimes steam blown into the mass ("wet steam") is preferred to dry steam. In this case there should be a compartment between the pan and the subliming-chamber, in which the condensed steam-water and a little melted naphthalene may collect.

The following apparatus for subliming naphthalene is described by Hirsch (*Chem. Zeit.*, 1884, p. 839):—Chamber A (Fig. 177) is made of 12-in. brickwork, standing isolated, 16 ft. long, 10 ft. wide, and 10 ft. high. On the brickwork rests a light roof frame, covered with roofing-felt. B is a wrought-iron pan, 10 ft. long, 3 ft. 3 in. wide, 19 in. deep, set over the curtain-arch C in such way that the fire-gases from the hearth D first travel towards the back, then rise in the flues E round pan B and then escape in the chimney, which need project only

3 ft. over the roof. In the flue E there is a damper for regulating the draught. F is a wooden charging-door, covered with sheet-iron on both sides, turning round the hinge G; during the sublimation this door is luted with clay. H H are two wood covers, covered with sheet-iron, loosely lying on iron stays fixed on the side walls; they act as dephlegmators, condensing the heavy oils whose vapours are carried along by the naphthalene vapours. J is an iron-covered door, luted with clay, for taking out the sublimed naphthalene. L is an iron air-pipe, 3 in. wide, projecting inside 4 in. and 18 in. above the roof; it carries the dish M, in which is collected the water condensing in L.

Some manufacturers state that it is better to mix the naphthalene with sand before subliming; but this seems quite unnecessary.

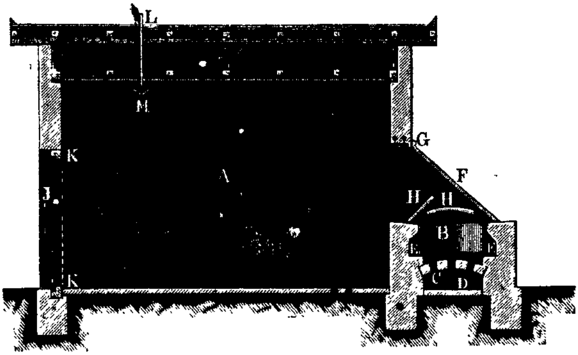

FIG. 177.

It has also been attempted to effect the sublimation by blowing in hot air by means of a fan-blast; but this has been discontinued. Ordinary air easily produces a fire; and a previous removal of the oxygen by passing the air through a coal-fire is too expensive. Moreover, the condensation is more difficult than when the heating is produced by indirect steam.

Rispler (*loc. cit.*) objects to all the plants for subliming naphthalene, published up to that time, that the work must be interrupted in order to clear out the chambers, which is a very disagreeable task for the men, and causes both loss of naphthalene and of heat. Moreover, it has the disadvantage that the sublimate is not of uniform grain; that which is formed first, when the chambers are cool, is a much finer powder than the coarser stuff condensing later on (which is preferred by the buyers). To avoid these drawbacks, he has designed a continuously working plant, consisting of two horizontal cylinders, like steam-boilers, fired from below, and a subliming-chamber, made of wood, and placed so as not to be in contact with any brickwork. The bottom of this chamber is formed by several funnels, open at the bottom and closed by jute bagging. Nearly all the sublimate collects in these funnels, which are emptied from time to time, without interrupting the work. The sublimate adhering to the sides and the top of the chambers need only be removed once *per annum*. Such a chamber of 12,000 cub. ft. capacity turned out 10 tons per month.

Examination of and for Naphthalene.

The properties of pure naphthalene have been described *supra*, p. 243. Commercial naphthalene is now required to be as nearly as possible chemically pure. It should have a pure, white colour, volatilize without any residue, fuse at 79°·6 to 79°·8, and boil at 217° to 218°, under a pressure of 760 mm. It should be free from any oily admixture, and soluble in petroleum spirit perfectly clearly, without leaving any residue.

According to present usage, the *fusing-point* of pure naphthalene is its *point of solidification*, determined by the method of Shukoff (*Chem. Zeit.*, 1901, p. 1111). That method is extremely accurate; the differences between the results obtained by various observers amount hardly to 0°·1. Shukoff's apparatus consists of a double-walled glass vessel, the space between the two walls being evacuated, and a thermometer, divided into tenths of a degree C., put into the vessel by means of a cork. The vessel is filled with fused naphthalene, heated only a few degrees above its fusing-point, and the thermometer is put in. The thermometer is at once covered by a layer of solidified naphthalene; the point at which its bulb turns shiny again is considered as the nearly correct fusing-point.

According to the prescriptions of the Union of German Producers of Tar Products, 150 to 175 g. of the average sample are liquefied in a porcelain beaker, holding 200 c.c., on the water-bath; while stirring with a copper wire bent in the form of a circle, the solidifying-point is read off on a thermometer, which indicates the temperatures between 60° and 90°, and which dips into the fused mass above the mark for 65°, in the just described way.

The examination for *oil* is carried out by exposing 50 g. naphthalene, wrapped up in several folds of thin filtering paper, and forming a parcel 10 cm. long and 7 cm. broad, with an outer cover of packing paper, at the ordinary temperature to a pressure of 150 atmospheres during ten minutes. The naphthalene is thereby converted into a hard cake, and any oil present is indicated by grease spots appearing on the filtering paper. Good naphthalene gives no or only very slight grease spots, which pass at most through one or two layers of the filtering paper. The naphthalene is bad if the oil spots are visible even on the outer wrapping paper.

The *sulphuric-acid* test is carried out as follows: 10 g. naphthalene is heated with 4 g. pure, concentrated sulphuric acid on the water-bath up to complete solution. The solution ought to be clear, and to possess a slight pink colour, which on heating to 180° ought to be changed at most into a light brown tint. Other 10 g. of naphthalene is dissolved in 22 c.c. pure concentrated sulphuric acid on the water-bath, furnishing a solution like that just described. Ten g. of this is diluted with 25 c.c. of water and cooled down to 15°; by gradually adding to it further 25 c.c. of water, neither a muddy appearance nor a precipitate ought to be produced.

A test for *constancy of colour*, that is for the absence of a yellow or red coloration when keeping the naphthalene on stock for some time, is sometimes made by the *nitric-acid* test. This is carried out by pouring pure, *not* fuming, nitric acid on the bottom of a desiccator and placing the naphthalene in a watch-glass above it, covering up the whole as usual. If the sample remains white for half an hour it is good, and if for two hours it is excellent. Inferior descriptions soon turn pink. After some hours all samples turn yellow, probably owing to the formation of nitronaphthalene.

The presence of *phenols* in naphthalene is discovered by boiling the sample with a dilute solution of caustic soda, cooling, filtering, and adding to the filtrate bromine-water and hydrochloric acid; any phenols present will now be precipitated as brominated compounds (*vide supra*, p. 798 *et seq.*).

Quinoline bases are discovered by dissolving the samples in concentrated sulphuric acid, pouring the solution into water, filtering, making the filtrate alkaline, and distilling, when the quinoline bases will pass over with the aqueous vapour, and will be recognized by their peculiar smell.

Häussermann (private communication to the author) points out that even a most thorough washing with acid and alkali does not free the naphthalene from certain other *hydrocarbons* which do not affect either the boiling-point or the other outward properties of naphthalene, but which make themselves felt in the subsequent manufacture of naphthylamine, naphthol, etc. These impurities are said to be removable only by certain solvents; but it would appear as if the hot-pressing of the naphthalene crystals, as it is now pursued at most works, equally tends to remove them.

Qualitative Test for Naphthalene.—In order to prove the presence of naphthalene, Vohl treats the substance in question with fuming nitric acid, adds a large quantity of water, washes the precipitated nitro-compound, and puts it into a boiling mixture of 1 part potassium monosulphide and 1 part caustic potash; traces of naphthalene yield a beautiful purple solution.

The quantitative estimation of naphthalene in commercial articles is nearly always based on its subliming property. Sometimes the *acidimetric estimation* described by Küster (*Berl. Ber.*, 1894, p. 1101) may be useful. It is based on the property of naphthalene to form an insoluble compound in molecular proportions with saturated solution of *picric acid.* The sample is placed in a small, strong flask, together with saturated picric-acid solution which fills it nearly to the neck. It is fitted with an indiarubber cork, through which passes a 7 cm. wide glass tube, closed at the bottom, but with a small lateral hole about 1½ cm. above the bottom. At first the tube is pushed down until the hole is free; the flask is evacuated by an air-pump, and the tube is then pulled up until the lateral hole is well within the cork. The flask is now heated on the water-bath until the reaction is complete; no naphthalene can escape during this time. After cooling overnight, the tube is lowered to admit the air; the contents are filtered, and the picric acid in excess is titrated with barium hydrate, using lacmoid as indicator. This process would also indicate acenaphthene, chrysene, and both naphthols, but not phenanthrene; it is, therefore only applicable where the former substances are absent.

The following special rules should be observed in this test. A picric-acid solution, saturated at the ordinary temperature, is about one-twentieth normal; a considerable excess of it must be employed, to ensure the quantitative formation of the molecular compound with naphthalene. The flask must be made of sufficiently strong glass to allow of its being evacuated from air without any danger of breakage. If the apparatus is properly constructed, the flask keeps for several days air-tight, so that it can be heated on the water-bath without producing any plus-pressure within.

The *estimation of naphthalene in coal-gas* is performed by Colman and Smith (*J. Soc. Chem. Ind.*, 1900, p. 128) by passing the gas through a dilute picric-acid solution, separating the naphthalene picrate and weighing it, or titrating the excess of picric acid by *N*/10 soda solution. Dickenson-Gair (*ibid.*, 1905, p. 1279) uses a similar method, but employs first dilute acetic acid, before the picric acid, of which a large excess must be taken. An improvement on this method, permitting the estimation by titration, is described by the same author later on (*ibid.*, 1907, p. 1263).

Fronsac (*Rev. chim. pure et appl.*, xvii., p. 4) also estimates the naphthalene in coal-gas by means of picric acid, measuring the picrate of naphthalene in a graduated tube.

White and Ball (*J. Gas Lighting*, lxxxviii., pp. 262 and 323), estimate naphthalene by picric acid, like the authors quoted above. To estimate its percentage in tar, they drive it out of this by a current of air at a temperature of 70° to 80° C. and pass the gases through two U-tubes, the first of which, also kept at 70° to 80°, is charged with CaO, glass wool, and P_2O_5, and serves for drying the gases. The second U-tube is placed in ice-cold water and serves for retaining and afterwards weighing the naphthalene.

Further papers on the picric-acid method for estimating naphthalene have been published by Jorrissen and Rutten (*J. Soc.*

Chem. Ind., 1909, p. 1179); Wien (*J. Gasbeleucht.*, 1911, p. 891); Albrecht and Müller (*ibid.*, 1911, pp. 592 and 594).

The estimation of naphthalene in the "spent oxide" of gas-works is performed by W. C. Davis (*J. Soc. Chem. Ind.*, 1914, xxxiii., p. 1120) by precipitating it with picric acid, and retitrating the excess of picric acid by caustic soda.

The estimation of naphthalene in the anthracene oil employed for taking out the small quantities of naphthalene contained in purified coal-gas, and sold by the name of "Röpert-Oel," is described in detail by Th. Hahn in the *J. Gasbeleucht.*, 1911, p. 1249.

Applications of Naphthalene.

The naphthalene occurring in large quantities in coal-tar (usually from 5 to 10 per cent., sometimes perhaps in excess of that[1]) was formerly one of the least welcome of its constituents. It generally accumulated in the creosote oil and caused inconvenience by crystallizing there; sometimes it led to the rejection of creosote oil for pickling timber (pp. 694 and 697). In such cases nothing remained but to work it into the pitch, or burn it for soot (*cf. infrà*, Genthe's German patent, No. 157542), or to employ it as fuel, mixed with coal. Even now crude naphthalene is sometimes employed as fuel in the melted state, for instance for heating the tar-stills. In that case the liquid naphthalene is injected into the fireplace by means of a steam-jet similarly to tar or tar-oils (pp. 324 *et seq.*).

The applications of naphthalene for the *manufacture of artificial colours* were formerly very few, in spite of a great many efforts in this direction; dinitronaphthol (Manchester yellow) and naphthalene red (Magdala red) were for a long time the only colours made from naphthalene. When the series of phthalein colours (eosin, etc.) was discovered, in 1876, a demand for phthalic acid sprang up, for which naphthalene is the starting-point. But far more important in this respect was the discovery of the long series of azo-colours, nearly all of which have come out since 1873. For most of these naphthols, especially $\beta C_{10}H_7(OH)$, are required, and for the preparation of these the purest naphthalene is demanded. Recently the manufacture of artificial indigo has been added to the above applications of naphthalene.

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[1] Exceptionally coal-tar is found containing hardly any naphthalene. Such has been the case with the Manchester Corporation Gas-works tar in 1873 and 1874, according to Watson Smith. He found naphthalene in cannel-coal tar, along with paraffin. On the other hand, Crace-Calvert states the percentage of Newcastle tar = 58 per cent. naphthalene, which is simply absurd.

One of the most important uses of naphthalene was for some time that for *carburetting gas*. This has been frequently proposed, *e.g.*, by Bowditch (B. P. 2937, 1862); but the principal impetus to this industry was given by the inventions of Livesey and Kidd, afterwards associated with H. Vale, of Hamburg (Ger. Ps. 2075, 8644, 9840, 19012, 32255). Their apparatus, called the "*albo-carbon light*," has been attracting much attention. It is principally adapted for small flames, and is stated to save more than half the gas consumed for the same illuminating power in the best argand burners; so that it is very economical, in spite of the cost of the naphthalene. It is a drawback that, if the apparatus is allowed to get too hot, there is too much volatilization of naphthalene and the flame burns smoky; if it were still further neglected, the naphthalene would boil and the apparatus would burst.

In experiments made by Mr John Pattinson (*Trans. Newcastle Chem. Soc.*, 1882, v., p. 135) 1000 cub. ft. of gas along with 4·63 lbs. of naphthalene, consumed in the albo-carbon lamp, yielded as much light as 2700 cub. ft. of gas, burned in fairly good flat-flame burners, or 1780 cub. ft. of gas in argand burners of good construction.

Elster (as mentioned in Schultz, *Steinkohlentheer*, 2nd ed., i., p. 199) found that 1 cbm. of Berlin gas, carburetted with 53 g. naphthalene, yielded 20-candle power, the hourly consumption per flame being about 100 litres and 5 g. naphthalene. Street-lamps consumed from 110 to 117 litres of gas along with 5 g. naphthalene, and yielded the light of 16 or 17 candles. On an average the albo-carbon light saved 50 per cent. in gas, and 30 per cent. in total cost. The best effect was produced with small burners. The specific gravity of the gas was raised from 0·38 to 0·60 by the carburetting process.

Fig. 178 shows the most usual form of albo-carbon lamp. The copper ball *a* is fixed on the socket *c* by means of a stem, *b*, the joint being made merely by true boring-out of *c* and turning *b*; *a* is closed by a screw-cap, *d*, which serves, for charging the naphthalene. The gas enters the ball through *c*, *b*, and *e*, and the burner *i* through *f*, *g*, *h*.

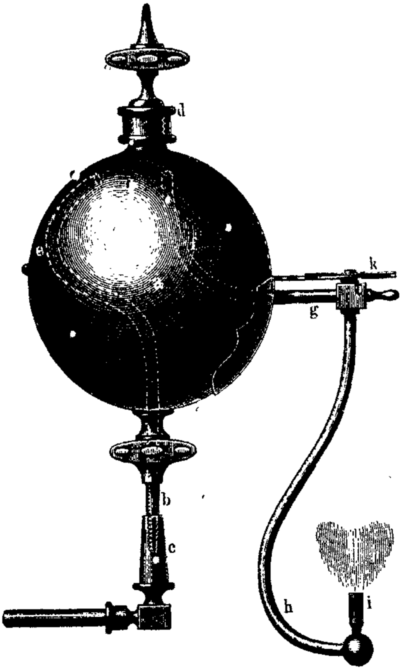

FIG. 178.

Above *i* is fixed the copper disk *k*, which is shown from above in Fig. 179. It will be noticed that by moving the slide *l l*, which revolves round a pivot in the centre, the disk *k*, cut out to correspond with *l l*, is either closed or opened.

The burning gas from *i* heats *k*, which transfers its heat to *a*, and heats the naphthalene contained therein a little above its melting-point, say to 80° or 90°. In consequence of this the gas passing through *a* is charged with naphthalene vapour, which greatly increases its illuminating power. If too much vapour is carried along and the flame begins to smoke, the slide *l l* is moved as in Fig. 179, whereby the heating of *a* is greatly diminished.

In spite of the advantages justly claimed, according to all appearance, for the albo-carbon light, the progress which it has hitherto made, although not inconsiderable (at one of the largest English tar-works the author was informed that in 1886 they made 400 tons of naphthalene sticks per annum for this object), is yet far from being so universal as might be expected; and it has even been abolished again in some cases where it had been introduced. This seems to be mostly owing to the trouble caused by the lighting of the gas. At the commencement, before the naphthalene has become heated, the light is inconveniently small, and some patience is necessary. On the other hand, if the apparatus is allowed to get too hot for one moment, the whole room is for a long time filled with the extremely pungent smell of naphthalene vapour. Of course this can be prevented by careful attention, but such is only too often wanting in the case of the domestics to whom the light must be trusted.

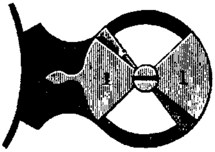

FIG. 179.

The principle of carburetting gas by means of naphthalene is evidently most excellent for enriching very poor gas, such as is obtained by abstracting the benzol from gas by one of the processes mentioned on pp. 64 *et seq.* Davis (*J. Soc. Chem. Ind.*, 1886, p. 5) mentions that such gas, from which 4 gall. of benzol had been extracted per 10,000 cub. ft., and which only possessed 9-candle power, was easily brought up to twenty candles by employing the albo-carbon light; whilst the consumption of gas for lighting a room 10 ft. square was brought down from 23 to about 3½ cub. ft. per hour. This process would also be adapted for making good illuminating-gas from the residual coke-oven gases (p. 158).

A new albo-carbon lamp has been constructed by Kitson & Co. (*Dingl. polyt. J.*, cclxvii., p. 34).

Philip's Carbo-Oxygen Gas (Wagner's *Jahresber.*, 1870, p. 728) is produced by the combustion of naphthalene, dissolved in petroleum, in a current of oxygen. A lamp suitable for this purpose has been described by Carl (*ibid.*, 1872, p. 856); but this process seems to be too troublesome and expensive.

J. W. Sutton (B. P. 4747, 1883) has constructed a somewhat similar apparatus; so also have W. G. Little (B. P. 17108, 1885); and H. J. Siebel, jun. (B. P. 2752, 1887).

Hempel (B. P. 6463, 1899) carburates spirit of wine by dissolving naphthalene in it. The light given out on burning this mixture is very strong and white.

Use of Naphthalene for driving Gas motors.—Chenier and Lion (Ger. P. 144942) employ the vapours of naphthalene and other solid hydrocarbons for heating, lighting, and motor engines. The naphthalene serving for driving motor-engines is employed in the shape of balls (*vide supra*, p. 836), which are liquefied, and the liquid is supplied to the apparatus for converting it into vapour or spray by means of an apparatus constructed for this special case. The motor is, just as in the case of any other heavy hydrocarbons, started with petroleum spirit; as soon as the change has been made for driving it by naphthalene, care must be taken that the cylinder is only moderately cooled. Some trouble may be caused by naphthalene solidifying in the pipe leading to the injector, and in the injector itself, during the stoppage of the motor-car, which necessitates liquefying the naphthalene before restarting; but this drawback is compensated by the low price and the absence of badly smelling outlet-gases. In comparative trials made during three days in Paris, the amount required for driving the motor-cars with naphthalene in balls (bought at the price of 20 francs per 100 kg.) was only 6 kg. per kilometer, and the cost 2 cent. per kilometer, against 14·7 litres of petroleum spirit (cost 8 cent.), or 14·8 litres of ordinary petroleum (cost 4 cent.), or 12·7 litres of slate-oil (cost 4 cent.). Quite as good results were obtained by the Hutton Co., Ltd., which has acquired the patent rights of Chenier and Lion for Great Britain. They found the best proportion to be used = 1 naphthalene vapour to 13 air. The experiments made with a stationary 12 h.p. engine, with 1000 revolutions per minute, showed the cost of driving this engine for an hour with petroleum spirit = 1s. 2½d., with paraffin oil = 9d., with naphthalene balls = 9d. The naphthalene may be used for this purpose in the crude or the partially purified state. It is also very suitable for driving motor-boats, according to the Hutton Company.

The Gasmotorenfabrik Deutz (Ger. P. 199205) applies naphthalene of the ordinary commercial quality for driving

Otto gas-motors, with the assistance of a water-bath for fusing it. The consumption is from 260 to 320 g. per h.p. hour, and the blowing-off gases are practically free from soot. Since technical naphthalene is an almost chemically pure substance, there are no resin-producing constituents which would cause obstructions in the valves and the piston (*Z. angew. Chem.*, 1907, p. 1264).

The Rütgerswerke (B. P. 7594, of 1908; Ger. P. 208380) employ for gas-motors a solution of naphthalene in one of the ordinary liquid fuels (say benzol), prepared by the aid of the waste heat of the motor, followed by pure fused naphthalene.

Richard Müller (*Techn. Rundschau*, 1910, p. 366) reports that the use of naphthalene has been proved to be very successful for driving explosion motors, and very cheap at a price of 80 mark per ton. Further communications on this subject have been made by Irinyi (*Stahl u. Eisen*, 1914, xxxiv., p. 1435; *Z. angew. Chem.*, 1915, ii., p. 7); and Bruhn (*Stahl u. Eisen*, 1914, p. 1691, and in *J. Gasbeleucht.*, 1915, pp. 581 and 714).

Use of Naphthalene as Disinfectant and Insect-killer.—Naphthalene is frequently employed for *keeping out vermin* (*e.g.*, moths) and in stuffing animal-skins; Pelouze[1] recommends it for disinfecting purposes generally, Fürbringer[2] especially for water-closets and sick rooms in lieu of carbolic powders. A special investigation of the antiseptic powers of naphthalene has been made by Ernst Fischer.[3] It stops the development of mould and kills the fungi in a very short time, as *Penicillium*, *Mucor*, *Phycomyces*, *Oidium lactis*, the fungus of yeast, the different schizomycetes, etc. Lower animals are driven away or killed; naphthalene therefore serves as a preventive against moths, Phylloxera, the insects destroying collections of beetles and butterflies, and any other vermin. Against itch a salve, consisting of equal parts of naphthalene and vaselin, does good service. Naphthalene is excellent for dressing wounds; it suits this purpose quite as well as, or better than, carbolic acid or iodoform, and it is not poisonous like these. It seems therefore called upon to play an important part in medicine and in the household. Furs and woollen clothing, preserved against moths during the summer months by means of naphthalene paper, pertinaciously retain the penetrating smell of naphthalene, and require *long* airing before they are fit to be worn.

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[1] *Bull. Soc. Chim.*, 1866, p. 351; 1868, p. 258.

[2] *Berliner klinische Wochenschrift*, 1882, No. 10.

[3] Schultz, *Steinkohlentheer*, 2nd ed., i., p. 109.

Salubrin (*Chem. Zeit.*, 1902, p. 850) is naphthalene, scented with a little nitrobenzol, to be used as a disinfectant.

Planner (B. P. 26983, 1898) fuses naphthalene or other tar hydrocarbons with camphor (equal parts), adds a disinfecting chemical, *e.g.*, potassium permanganate, and moulds the mixture in a proper way. Or else he cools the naphthalene, reduces it to powder, mixes it with the permanganate, and then fuses the mixture as above.

Combination of Naphthalene with Sulphur.—According to an observation made by H. Köhler (Ger. P. 192815 and patents in other countries taken out for this process by the Rütgerswerke-Aktiengesellschaft), sulphur easily dissolves in every proportion in fused naphthalene, and on cooling crystallizes with it in an isomorphous mixture. If equal weights of both these substances are fused together (which exactly corresponds to 1 molecule naphthalene + 4 atoms sulphur), and the solidified surface of the mixture is perforated before the mass has cooled down, the vessel is found filled with long, scaly crystals of the colour of sulphur, consisting of naphthalene and sulphur in the proportions employed. When left lying in contact with air, the naphthalene evaporates, leaving the sulphur behind in an extremely finely divided form. The naphthalene can also be dissolved out of the mixture by appropriate solvents which do not dissolve the sulphur, *e.g.*, alcohol, petroleum spirit, etc., and in this way sulphur is obtained in molecularly fine form, just like the well-known precipitated sulphur. The sulphur comes out in even more finely divided form, if the liquid solution in naphthalene is not allowed to crystallize, but is suddenly cooled down, *e.g.*, by pouring it into cold water, with agitation. This product, sold as naphthalene-sulphur, has been successfully employed for destroying the *Oidium Tuckeri*, the *Tortrix pilleriana*, etc., infesting the vines (Haack, *Z. angew. Chem.*, 1909, pp. 817 *et seq.*).

Various other uses of Naphthalene.—Sometimes, according to *Chem. Trade J.*, 1891, p. 304, naphthalene is employed for *pickling timber* by leaving it for an hour or two in a box filled with melted naphthalene. It is said to protect the timber against moisture and insects, but it is not equal to creosotizing for pit-props or for use in water.

Heinrich (Ger. P. 99710) employs naphthalene for a preliminary *tanning* of skins, together with ordinary tanning solutions. It is also used for denaturing dried sheep's intestines, to be imported into Germany.

Sudheim and Koppen (Ger. Ps. 6051 and 7784) employ naphthalene in the manufacture of non-phosphorous *matches*.

Pantopollite is dynamite containing a few per cent. of naphthalene. It was supposed to prevent the formation of nitrous fumes during the explosions; but practical trials have shown that the smell remaining after the explosion was far worse than in the case of ordinary guhr-dynamite (Wagner's *Jahresber.*, 1876, p. 495).

Naphthalene or its nitro-compounds are also essential constituents of various other explosives, such as "Dahmenite," etc., described in the German patents, 93228 (Geserich), 93351 (Bielefeldt), 100522 (Corbin & Co.).

S. Stein (Ger. P. 23947) makes *porous stoneware* by incorporating with the clay naphthalene suspended in water or suitably dissolved, drying, volatilizing the naphthalene and recovering it at the same time, whereupon the clay is burned in the usual manner. The burned articles show an even porosity; and as the naphthalene does not leave any ash, the pores are not partly filled up with a fusible mass, less capable of resisting changes of temperature.

M. E. Coutin (*J. Soc. Chem. Ind.*, 1884, p. 353) makes a specially "*detergent*" *soap* by melting two parts of ordinary soap with three parts of naphthalene. [While it is very doubtful whether such a soap will remove dirt better than the ordinary article, it is certain that those using it will produce an intensely disagreeable atmosphere around themselves!]

According to Callenberg (*Prometheus*, 1902, p. 96), naphthalene, if added to the artificial camphor used in the manufacture of celluloids and dynamites, makes these uninflammable and inexplosive.

Traine (Ger. P. 154756) employs a solution of naphthalene in linseed oil in the presence of rosin, as varnish. This product is more liquid than ordinary varnishes, and is not turbid, but remains clear; nor does it form skins on the surface through the oxidizing action of the air.

Köhler (Ger. P. 204256) also employs naphthalene as an excellent and cheap solvent for asphalte, resins, and sulphur.

Kreis (*Chem. Zeit.*, 1905, p. 714) reports that in Basel naphthalene is sold by the name of "Gasin" for increasing the illuminating power of petroleum, and as "Rhodin" for the extermination of vermin.

Genthe (Ger. P. 157542) burns naphthalene to obtain *soot*, by means of a water-cooled burner.

An observation made by Grabowsky (*Berl. Ber.*, vii., 1605), according to which naphthalene reacts with formaldehyde and methylate (with production of diphenylmethane), has been taken up by the Badische Anilin und Sodafabrik, B. P. 16245, of 1908; Ger. P. appl. B48200; *Chem. Zeit. Rep.*, 1908, p. 325) for the *production of artificial resins.* Since these resins are not soluble in alcohol, they cannot replace shellac in all cases (Weger, *Z. angew. Chem.*, 1909, p. 338).

Buss and Fohr (Ger. P. 186396) employ naphthalene, in lieu of pitch, for converting coal dust into "patent fuel."

Perlewitz (Ger. P. 286846) agglomerates saw-dust by fused naphthalene.

The Rütgerswerke Aktien-Gesellschaft employ it in the manufacture of india-rubber goods (Ger. P. 214518), and for producing elastic, plastic masses from thickened oils (Ger. P. 224040).

Statistics.

We can give such only for Germany, where the Deutsche Teerprodukten-Vereinigung (Union of German tar-works) has collected the following data from its members, proving that the sales of naphthalene are considerably below the quantity producible in the tar-distillation; hence part of it is left in the heavy tar-oils, or employed in the crude state as fuel, etc. The figures mean metrical tons (at 1000 kg.).

	1909.	1910.
Tar worked up by the members of the Union	825,000	895,000 tons
Naphthalene producible from this (calculating it = 5 per cent.)	41,250	44,750 „
Sales of pure naphthalene	23,300	29,200 „
„ crude „	6,000	6,200 „
Total sales	29,300	35,400 „
Expressed in per cent. of the tar	3·51	3·95 per cent.
Leaving an unsold balance of	30	20 „

Importation of naphthalene into and exportation from Germany (tons).

	Importation.	Exportation.
1903	14,480·6	2332·7
1904	12,443·6	2878·2
1905	11,645·2	2735·2
1906	8,113·8	2823·2
1907	10,145·9	5966·2
1908	8,343·2	4183·9
1909	7,774·5	6346·8
1910	4,996·6	9228·1
1911	4,88[illegible]	9302

According to Stone (*Chem. Ind.*, 1915, suppl., p. 338), the United States before the great European War produced about 2½ million lbs., nowadays about 7 million lbs. of naphthalene per annum, their normal consumption being about 9 million lbs.

Acenaphthene.

Properties, p. 248.

According to the Ger. P. 277110 of the Gesellschaft für Teerverwertung, the crystals of crude acenaphthene separating from the runnings following the naphthalene fraction, which contain, besides acenaphthene, other solid constituents, are subjected to a redistillation, with a suitable amount of liquid constituents of coal-tar going over between naphthalene and acenaphthene.

CHAPTER VIII

CREOSOTE OIL

In this chapter we treat of the employment or further refining of those distillates from coal-tar which are midway between carbolic oil and anthracene oil. These are, in the first place, the fraction of coal-tar distilling directly between 240° and 270°, and besides, from either side, the residues from the manufacture of carbolic acid, naphthalene, and anthracene. Practically everything which cannot be used for any other purpose is run into the creosote-oil well.

Formerly the only treatment of this oil consisted in separating the crude naphthalene crystallizing out from the liquid portion. It was generally assumed that it is not possible to prepare good naphthalene and good phenols from this oil, which was employed in its original state for impregnating (pickling) timber, and into which everything was thrown which could not be used for any other purpose. The solid substances separating out, and consisting mainly of naphthalene, were sold at a low price for the purpose of manufacturing lamp-black (*vide infra*).

In the course of time, however, processes have been worked out by which phenols and naphthalene can be extracted from creosote oil, of the same quality as those obtained from the "carbolic oil," which will be treated in the next chapter. On the other hand, the prescriptions imposed by the public bodies for the quality of the impregnating-oil have become more and more stringent, so that it is no more possible to sell that fraction in the state in which it is obtained in the first distillation of coal-tar. Hence it is worked up by repeated distillations in apparatus of greater efficiency than the stills in which the tar is submitted to the first distillation.

Properties.—Creosote oil, also called heavy oil or dead oil, is, in the fresh state, of a light greenish-yellow colour and strongly fluorescent, and is rendered still more fluorescent by the action of air and light. After some time it turns much darker and appears bottle-green by reflected, dark red by transmitted light. As the distillation proceeds, it becomes gradually darker and more consistent. Its smell is extremely characteristic—unpleasant, almost nauseous; it is probably caused by sulphur compounds not yet isolated. It is as thick as ordinary fatty oil, and at first has also an oily touch, but soon acts upon the skin by its acids. It is always heavier than water; the specific gravity of its last portions is 1·070. The average sp. gr. is about 1·04.

Composition.—The following bodies have been found in creosote oil:—Naphthalene, α- and β-methylnaphthalene, tetrahydronaphthalene, diphenyl, acenaphthene, anthracene, phenanthrene, and the hydrocarbons coming in between these; phenol, cresol, more especially xylenol and α- and β-naphthol; aniline, quinoline, isoquinoline, and all the other bases mentioned in Chapter III. (pp. 293 *et seq.*). Only few of these substances are liquid, and it is certain that many more substances of a low fusing-point, as yet undiscovered, must exist in the liquid part of creosote oil.

We get an important insight into the nature of creosote oil (as well as anthracene oil) by the following results, obtained by Watson Smith from the distillation of Lancashire tar. Sample No. 1 was taken after 150 gall. had come over; No. 2 was a sample of the next 100 gall.; No. 3, of the next 100 gall.; No. 4, of the first "red oils"; No. 5, of the last oils.

No. 1 was of light colour, and on cooling was almost entirely solidified by the crystallization of naphthalene.

No. 2. Yellowish oil, with few crystals of naphthalene.

No. 3. Quite similar.

No. 4. Red oil, with but little deposit.

No. 5. Red oil, solidifying on cooling.

All contained a little water. Each of the samples was distilled, with the result given below, in percentages by volume (N signifies that, on cooling, naphthalene began to crystallize; O, that all remained liquid; A, that anthracene began to crystallize).

Temperature.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Up to 180°	1·0	...	6·6	1·0	2·7 O
,, 210°	6·3 N	...	4·7 N	2·0	1·1
,, 220°	10·0	16·0 N	1·6	8·3 N	0·7
,, 230°	12·0	5·5	7·6	2·0	0·7
,, 240°	14·3	13·8	1·8	4·7	0·9
,, 250°	13·[illegible]	9·8	8·3	... O	3·3
,, 255°		...	...	...	...
,, 260°	9·3	4·9 O	9·3	9·7	0·7
,, 270°	7·0 O	8·9	1·6 O	12·0 A	1·8
,, 280°	4·3 A	4·9 A	8·7	8·7	1·8 A
,, 290°	3·7	3·5	6·6 A	5·4	1·8
,, 300°	3·7	3·8	11·3	4·3	5·9
,, 310°	3·7	2·1	4·5	3·0	12·0
,, 320°	3·7	2·8	1·3	7·3	8·2
,, 330°	...	...	...		4·0
,, 335°	...	...	...	6·0	
,, 340°	...	2·8	...		
,, 345°	...	...	...		
,, 350°	...	2·1	...		
,, 360°	...	...	1·6	18·0	
Above 360°:—					
Yellow crude anthracene	7·1	4·8	18·0	...	34·0
Orange or red substance	...	1·8	4·3	5·3	16 0
	99·4	87·5	97·8	97·7	95·6
State of the pitch remaining behind on rectification	good	very good	half coked	hard	beginning to coke
TOTALS.					
Crystallizing naphthalene oils	66·2	45·1	33·3	15·0	0
Not crystallizable oils	7·0	13·8	10·3	9·7	11·9
Anthracene oils	26·2	28·6	47·6	70·0	83·7

Church and White (*J. Ind. Eng. Chem.*, 1914, vi., p. 396) describe tests for estimating the *paraffins* contained in coal-tar creosote, either by sulphonation or by means of dimethyl sulphate.

Storing-up of the Creosote Oil.

Since there are often very large stocks of this oil accumulating at the works, there must be correspondingly large store-tanks or wells, which in many cases are not covered up, as the oil is not very volatile and the rain-water floats on the top of it, whilst the pumps take it away from the bottom. Still it is safer, as a precaution against fire, to cover up the tanks. At La Villette, the creosote oil is kept in large upright cylindrical tanks, standing on brick pillars over a water-tank visible and accessible from all sides. Thus any leakages are noticed at once, and in any case the oil is prevented from penetrating into the ground. Where this is of no great consequence, the oil-tanks are, as a rule, partially or entirely sunk in the ground. They are better if made of boiler-plate than of brickwork set in cement.

It is advisable to fix a steam-pipe in the well, so that the naphthalene crystallizing out can be dissolved again before any large quantity is sent out.

The store-tanks mostly have a flat bottom, and a conical or dome-shaped top, with a (loosely covered) manhole at the top and a lightly closed manhole just over the bottom, serving for getting out the solid matter when cleaning the tank. If they are not within the active zone of a lightning rod, they ought to be protected by such a rod. In Germany, according to the official rules for the storing of inflammable liquids, every tank must be moreover surrounded by an earth wall, at such a distance and such a height, that the annular space between the wall and the tank suffices for holding three-quarters of the contents of a tank. Of course on laying out the plant, these store-tanks are placed so as to be as little as possible exposed to danger from fires breaking out in the factory.

The Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft (*Petroleum*, 1911, p. 724) has worked out a plan, by which it is assured that in case of an excessive pressure occurring within a tank (which may lead to the top being torn off from the cylindrical part by the explosion) certain distinctly defined parts of the cover are removed, thus preventing a complete destruction of the tank and the consequent breaking out of a great conflagration.

Directly after the distillation, the creosote oil is pumped or forced into these tanks, where it is allowed to cool, and where most of the *naphthalene* separates. Creosote oil rarely contains less than 40 per cent. naphthalene, sometimes more. It therefore solidifies to a great extent on cooling, and usually exhibits a dense, continuous covering of naphthalene. Oil obtained from tar, produced from material containing much cannel-coal, contains less naphthalene and more of the higher phenols. The bottom of the coolers is provided with a tap, which before the entrance of the oil is closed by means of a wooden plug. After cooling, this plug is removed and the liquid portion of the oil is now conveyed into the principal reservoir. The naphthalene is shovelled out into drainers; its further treatment will be described later on. Some people consider this naphthalene from creosote oil as unsuitable for purification, and only fit for softening the pitch or burning into soot. But this is a prejudice; by proper treatment it can be purified as well as the naphthalene from carbolic oil.

Carriage of Creosote Oil.

On a comparatively small scale creosote oil is conveyed in wooden casks, which are very liable to leak unless they have been previously saturated with a solution of glue. On a larger scale exactly the same contrivances are employed as for tar itself, viz.:—for railway carriage, block waggons with cylindrical or angular wrought-iron tanks holding 10 or 15 tons; for water carriage (on rivers or canals), tank-boats. Even more than for the carriage of raw tar it is necessary in this case to provide the tanks with heating arrangements (closed steam-coils), in order to liquefy their contents when solidified in the cold of winter.

Redistillation of Creosote Oil.

This operation was for a long time avoided at most tar-works, as causing more trouble and expense than it was worth, and it was principally performed at some of the Scottish works. Recently it has come into more general use on the Continent. Its object is, of course, to separate as much of the more valuable constituents as possible.

The redistillation of creosote oil is usually performed in stills just like ordinary tar-stills; possibly in some cases with the employment of a vacuum. When distilling under ordinary atmospheric pressure, we obtain at first a very little "light oil" like that described on p. 445, then a little more "carbolic oil," but principally what may be called the first and the second "naphthalene oil," the limit between these being taken when the thermometer indicates 210° to 215° C. The "first naphthalene oil" on cooling solidifies to a great extent into naphthalene, almost of pure quality, about which we shall say more in the next chapter. The "second naphthalene oil," boiling up to 280°, also separates much naphthalene on cooling, but in a less pure state, containing methylnaphthalene and acenaphthene. The residue left in the still contains a little anthracene, and is worked up with the anthracene oil, as described in Chapter VII.

When the "first naphthalene oil" has cooled down, the solidified naphthalene is separated from the *liquid oily portion* (which may amount to one-half or a little more of the whole). This filtered oil contains, besides hydrocarbons, a few per cent. of tar bases which may be extracted by an acid, and a large quantity, say 25 per cent. of *phenols.* These make it valuable for disinfecting purposes, but in its crude state it would be frequently inconvenient to apply. We shall see below how this is remedied by the production of emulsions, etc.

Sometimes the "first naphthalene oil" is again redistilled, in order to obtain products containing a higher percentage (up to 50 per cent.) of phenols, which are employed for disinfecting purposes, or as an addition to the solution of zinc chloride for pickling timber.

The "second naphthalene oil" is also, after cooling, separated into a solid portion (impure naphthalene, *vide supra*), and a liquid portion which is employed for pickling timber as described below.

Wurtz (*Matières colorantes*, p. 33) recommends the following treatment:—The heavy oil is distilled in boilers holding 1000 to 2000 litres; and the following fractions are collected: 1st, the products below 120°, which go to crude benzol; 2nd, the products between 121° and 190°; 3rd, the residue, which goes back to the tar. The second fraction [between 121° and 190°] is washed with acid and alkali, and is then sold for lubricating, or for pickling timber, or else it is converted into an illuminating-oil. For this purpose the naphthalene should be removed by treating with 10 per cent. concentrated sulphuric acid, then with water, then with 6 per cent. concentrated solution of caustic soda. The oil is now rectified; and the distillate is agitated with ferrous sulphate (*vide infra*). The oil thus purified is sold as "huile sidérale."[1]

According to Rispler, it is best to run the creosote oil directly from the distillation of the tar into cooling-pans, where the crude naphthalene crystallizes out. The liquid portion is used for pickling timber. The crude naphthalene is redistilled in ordinary stills, without a column at the top. Generally only one fraction is made up to 250°, which goes into cooling-pans. If two fractions are made, No. I. is that passing over up to 230°; No II. from 230° to 250°. In a special instance, No. I. amounted to 39·75 per cent., No. II. to 27·30, together 67·05 per cent. The naphthalene obtained from No. I., pressed in the cold state, showed a solidifying point of 78°·6, and the following boiling-points:—90·45 per cent. at 214° to 220°; 4·60 per cent. at 220° to 230°; 1·20 per cent. at 230° to 250. The cold-pressed naphthalene from No. II. had a solidifying point of 78°·5, and boiling-points:—81·25 per cent. at 214° to 220°; 10·46 per cent. at 220° to 230°; 3·46 per cent. at 230 to 250°. By redistilling the residue a product was obtained, yielding at 230° to 250° 7·3 per cent. distillate with a solidifying-point of 72°·6.

It seems to be a better proceeding (as also pointed out by Spilker) to pump the crude creosote oil before it has had time for cooling and separating its solid constituents into the creosote-oil stills, which are exactly like the tar stills in respect of size and shape, and to distil it by open fire, fractionating for carbolic oil, naphthalene oil I. and naphthalene oil II. The oil is distilled like tar, in a vacuum, and with partial application of a column, as will be described in the next chapter in connection with the distillation of the middle oils. The following fractions are taken:—

Carbolic oil	up to 195°
Naphthalene oil I.	from 195° to 230°
Naphthalene oil II.	„ 230° „ 280°
Anthracene oil	Residue

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[1] I have not been able to discover that any "huile sidérale," made in the way described by Wurtz or in any similar manner from coal-tar oils, is sold anywhere. It is possible that in this case again there has been some confusion with paraffin oils: but even if it be otherwise, we can only say that the above process must have been discontinued long since, as at the present prices of illuminating-oils it could not possibly be remunerative.

The first two fractions go into the cooling-house, together with the same fractions of the middle oil; the residue is worked up together with the anthracene oil, or placed in a special reservoir, together with the oily by-products of the manufacture of anthracene and naphthalene, and serves for the manufacture of "prepared tar" (*supra*, p. 549), of impregnating-oils, fuel-oil, oil for Diesel motors, and similar purposes; or else for the manufacture of soot (lampblack); *vide infra*. A good many patents have been taken out for improving this oil for the just-mentioned purposes, and for using it up in other ways, as we shall see later on.

In creosote oil from gas-tar, Rispler (*loc. cit.*) found about 28 per cent. naphthalene and 16 per cent. acid oils; in that obtained from coke-oven tar, about 32 per cent. naphthalene and 10 per cent. acid oils.

Special Processes for treating Creosote Oil.

Rohart (Ger. P. 14924) heats heavy coal-tar oil, crude petroleum, etc., mixed with lime, in a still for several hours, and then submits the mass to distillation.

Frank (Ger. P. 139843) heats completely dehydrated coal-tar oil with 5 to 10 per cent. brimstone to 220° to 250°, until the evolution of H_2S ceases and a deep brown oil has been formed which is much more viscid, less volatile, and has a stronger preserving and disinfecting power than the original oil.

Seidenschnur (*Chem. Zeit.*, 1909, p. 701) asserts that the phenols possess antiseptic properties only in aqueous solution, but not when dissolved in tar-oils, in the shape of creosote oil, etc. Coal-tar oils, after being deprived of phenols, have exactly the same bactericidal action as before. The antiseptic properties of anthracene oil are even superior to those of lower-boiling tar-oils. Petroleum oils have no antiseptic power unless a little sulphur has been dissolved therein in the state of boiling.

The *pyridine bases* are sometimes removed from creosote oil by a special treatment, but we must refer for this to the next chapter, especially as these bases form a valuable constituent in creosote oil for preserving timber (*vide infra*), and therefore ought not to be removed from it when using it for that purpose

Removing the Smell.—To remove the disagreeable smell of tar-oils used for disinfecting purposes is the object of various inventors. This nauseous smell is principally caused by certain sulphur compounds. A very common proceeding is shaking up with a solution of *ferrous sulphate*, say 4 per cent.

The Rütgerswerke-Aktien-Gesellschaft, at Berlin, employ for this purpose the *acetate of lead*. According to their Ger. P. 153585, a solution of 100 kg. normal or basic lead acetate in 450 kg. water is added to 10,000 kg. anthracene oil or other heavy tar-oils. The mixture is heated in a still to 180°, and superheated steam is passed through, until about 20 to 25 per cent. of the oil has been driven off and condensed. The oil remaining in the retort has a fine colour and very little smell; the receiver contains a distillate of bright colour fit for burning as fuel or for driving motor-cars. The blowing-in of steam during the distillation is indispensable; if the heating is effected entirely by an ordinary fireplace, the oil remaining in the retort does not lose its bad smell and easily separates crystals. The same effect is obtained by means of other lead salts, or of copper salts, but lead acetate is the cheapest. The idea of employing lead or copper salts for this purpose is not new (*cf.* Ger. Ps. 43145 and 107239; and U.S. P. 378246), but the result is unsatisfactory unless the process is carried out as just described.

Another patent of the same firm (Ger. P. 147163) for removing the bad smell of tar-oils prescribes adding to 10,000 kg. of the oil 20 kg. of an *aldehyde* or *ketone*, preferably *formaldehyde*, and some acid or alkali; heating by steam to about 90° for some time. The aldehyde acts upon the smelling compounds, water being separated, and condensation products, possessing little or no smell, being formed and remaining in the oil. By continuing the heating, a few per cent. of more volatile compounds are driven off. The remaining oil, apart from the improvement of colour and smell, possesses some further advantages in comparison with the ordinary impregnating-oils. It is more viscid, has a higher specific gravity, and contains less volatile substances, so that there is less danger of fire when employing it.

Deichler applied for a German patent (appl. D14576) for treating heavy tar-oils with formaldehyde for the purpose of removing the smell, but the patent was refused, as colliding with the just-mentioned patent of the Rütgerswerke.

According to a further patent of the Rütgerswerke (Ger. P. 223868) the tar-oils are treated with sulphuric acid of 50 to 60 per cent. H_2SO_4, whereby at 80° to 90° a portion of the badly smelling compounds is separated in the shape of acid-resin, and easily removed. *E.g.*, 1000 kg. creosote oil is heated in a lead-coated vessel provided with agitating-gear, to about 90°, and 100 kg. of sulphuric acid of 60 per cent. H_2SO_4 is gradually added with constant stirring. After some time of heating, the mixture is allowed to cool, the oil is drawn off from the acid and the acid-resin, and washed with 100 kg. caustic-soda solution of sp. gr. 1·3 or more or less, according to the nature of the raw oil. The oil is then heated to 100° and steam passed through until no more naphthalene goes away.

A patent of the Gewerkschaft des Steinkohlenbergwerks "Lothringen" at Gerthe, in Westphalia (Ger. P. 213745), prescribes adding to the oil small quantities of carbon tetrachloride, with a little hydrochloric acid, heating to 200° to 300° and driving off part of the product of the reaction. When employing rather more carbon tetrachloride, the addition of hydrochloric acid and the partial distilling off may be omitted. Thus an oil with very little smell, of a fine brown colour and great viscosity, is obtained, as desirable for impregnating purposes.

Melamid and Grötzinger (B. Ps. 9856 of 1912; 5484 of 1913; Ger. Ps. 264811, 276765, 278192; Fr. P. 443650) convert the hydrocarbons of tar-oils into hydrocarbons of lower boiling-point by heating with phosphoric acid.

Creosote Oil and Preparations from it as Antiseptics.

Creosote oil contains from 10 to 20 per cent. and sometimes more than this of phenols, of which very little is carbolic acid, but mostly cresols and higher homologues. Even in the crude state it is an excellent antiseptic and is extensively used as such, in spite of its unpleasant smell and its slight solubility in aqueous liquids. Dusart has shown the strongly antiseptic properties of the portions distilling between 210° and 300°, when freed from naphthalene. Before a separate fraction was taken in tar-distilling, which contains most of the phenols, together with naphthalene, pyridine bases, etc., of which we shall treat in the next chapter, it was usual to convert the creosote oil as a whole into a disinfectant, by various processes. Most of these are now applied to the crude carbolic oil, or even better to the crude mixture of cresols, from which carbolic oil on the one side, and naphthalene, etc., on the other side, have been removed. We shall therefore describe them in the next chapter under the heading: "Preparations from carbolic acid and cresols."

A *disinfecting powder* is obtained from creosote oil or "first naphthalene oil" by mixing it with about four times its weight of dry hydrated *lime* (preferably quicklime which has been hydrated by lying in the air and fallen into powder). This mixture after a short time takes a brick-red colour, by the formation of rosolic acid, etc., and is much employed in stables, railroad cars, etc., etc.

Instead of employing creosote oil by itself, it has become very usual to combine with it the action of other antiseptic agents, in the first place *chloride of zinc*, which for a long time has been employed by itself for the pickling of timber (*cf. infra*, p. 679). This has been done for many years at the various factories owned by the Rütgers Company. A special form of such a combination is that patented by Guissani (Ger. P. 132202), who first removes the moisture from the wood by keeping it in a vacuum in a high-boiling liquid, and then dips it in an open vessel in creosote oil of sp. gr. 1·09, overlaid by an aqueous solution of zinc chloride of sp. gr. 1·02. Emulsions of creosote oil with solutions of zinc chloride are described by the Berliner Holzkomptoir (Ger. Ps. 139441 and 152179).

Emulsions of Creosote Oil or Distillates therefrom.

A serious drawback of the use of the raw tar-oils is their slight solubility in water or aqueous liquids generally. This drawback is overcome by mixing the oil with a concentrated solution of *soap*, more particularly the soft potash-soap, which partly dissolves them, and partly converts them into *emulsions*, wherein the oil is contained in a state of extremely fine division.

According to Engler and Dieckhoff (*Arch. Pharm.*, 1892, part 8), already in 1874 solutions of soap in tar-oils, or of tar-oils in soap, were found in the trade. Such solutions form with water an emulsion in which the tar-oil is in the state of finest division, or they are even completely soluble. The first manufacturer whose preparations (called "Sapocarbol") were scientifically examined was I. Schenkel, of Eisenbüttel (*Pharm. Centr.*, 1884, p. 290), in 1884; but it was only in 1887, when the Creoline of Jeyes was extensively advertised by Messrs William Pearson & Co., of Hamburg (hence called "Creoline Pearson"), that these articles became generally known (Ger. Ps. 65387, 65533 to 65537).

Creoline (also sold as *cresolin*, *disinfectol*, etc.) is a dark-brown syrupy liquid, smelling of creosote, sp. gr. 1·04 and 1·08, soluble in every proportion in dilute spirit of wine (1 : 7), ether, and chloroform, partially in petroleum spirit, but insoluble in methylic alcohol. With water it forms an emulsion, most perfectly in the proportion of 2·5 per cent. creoline, of faintly alkaline reaction; it makes no spots and is not poisonous, even when 5 per cent. strong. With acid or alkaline water, or with glycerin, more darkly coloured emulsions are formed. Creoline is used in the same way as carbolic acid. The first observers who recognized Pearson's creoline as a soapy tar-oil solution were Otto and Beckurts (*ibid.*, 1889, p. 227); the results of Sprenger (*Z. angew. Chem.*, 1891, p. 183) in the main agree with theirs, as proved by the following table. According to this, creoline is nothing but a mixture of creosote oil with a soda-rosin soap and water.

	Otto and Beckurts.	Sprenger.	
Hydrocarbons	59·60	44·94	per cent.
Phenols	10·40	12·67	,,
Pyridine bases	0·80	2·76	,,
Abietinic acid (rosin)	23·00	32·45	,,
Water	3·40	5·34	,,
Soda	2·80	1·45	,,
Sulphur	...	0·25	,,
Chlorine	...	0·14	,,

From the very interesting research of H. Collier (*Pharm. J. and Trans.*, 1890, xxx. p. 751), on the emulsive properties of rosin soap, we learn that soap manufactured by two hours' boiling of 112 g. rosin with 20 g. caustic soda and 580 g. water is able to convert even mercury, on shaking, immediately into the state of finest division, and that oils, chloroform, thymol, camphor spirit, creosote, etc., are quickly and completely emulsionated by adding a small quantity of rosin soap.

From the above analyses we see that the creoline analyzed by Otto and Beckurts was made with 30 parts of rosin, which was saponified and dissolved in 70 parts creosote oil; whilst the article analyzed by Sprenger was made from 40 parts rosin and 60 of creosote oil. This, as well as further analyses, prove that the "creoline" of trade has been very differently composed at different times; and this is still further proved by the existence of other creolines (such as Ortmann's Ger. P. 51515, 1889), in which the emulsion of creosote oil is effected by the addition of solutions of gum arabic, or of certain sulphonic acids of heavy hydrocarbons.

Quite a number of coal-tar preparations, sold for antiseptic purposes, go by the name of "creoline." Their value is very unequal, and properly speaking they should be tested by their bactericidal action.

According to Baroni (*Giorn. Farm. Chim.*, li., p. 289), good creoline is a brownish-red, clear liquid, smelling of coal-tar, not unpleasantly, sp. gr. 1·03 to 1·08, yielding in the proportion of 1 : 40 a milk-white emulsion which keeps for weeks. Good creoline contains from 2·5 to 4·5 per cent. NaOH, partly saponified, and 70 to 80 per cent. coal-tar oil (a sample of Pearson's creoline showed 78 per cent.), as extracted by ether. The percentage of phenols is about 20 per cent. Creoline is prepared by saponifying the rosin with a solution of caustic soda, sp. gr. 1·332, at 100° C., adding the coal-tar oil, previously heated to 70° or 80°, mixing at 100° and filtering. Baroni quotes the following proportions for various qualities of creoline:—

	Venetian turpentine.	NaOH solution, 1·332 spec. grav.	Coal-tar oil, spec. grav. 1·08 to 1·035	Colophonium rosin.	Beef suet.
	Grms.	Grms.	Grms.	Grms.	Grms.
1. Italian creoline	250	70	775	...	...
2. Ordinary creoline	...	90	780	200	...
3. Solid creoline, f.-p. 55° to 56°	70	90	750	60	80

The following table shows the composition of two commercial creolines of good quality, besides that of "Italian Creoline":—

	NaOH.			Coal-tar oil.	B.-p. of coal-tar oil. °C.	Phenols and cresols.	Rosin.
	Not Saponified.	Saponified.	Total.				
Creoline A .	1·76	0·96	2·72	77	180 to 270	12	17·5
Creoline B .	2·96	0·32	3·28	66	170 ,, 260	16	27·3
Italian Creoline	1·84	0·76	2·6	76	160 ,, 270	16	19·0

In Germany the designation of "creoline" was officially restricted in 1903 to the "Creoline Pearson," *supra*, p. 658.

Lysol is a preparation extensively employed, because it is perfectly soluble in water. Such a preparation was first made by Schenkel and sold as *sapocarbol.* Lysol itself, according to Dammann's patent (Ger. P. 52129), later on cancelled by a decision of the German Reichsgericht, is made by mixing tar-oils, rich in phenols and cresols, with linseed oil or rosin, and saponifying the oil or rosin by caustic potash solutions and spirit of wine, heating with a reflux cooler until the mixture is homogeneous. Thus brown, oily, viscous, translucent liquids or semi-solids are obtained, easily soluble in pure water.

According to Gerlach (*Chem. Zeit.*, 1890, p. 1289), lysol is made from the first portions of creosote oil, passing over between 199° and 201° C.; these contain mostly phenol and cresols, and scarcely any neutral oils.

Reuss (*Chem. Ind.*, 1897, p. 8) gives the following analyses of lysol:—

Constituents.	Brand "Elsenbuttel."	Brand "Schulke & Meyer."
Pure cresols . . .	49·20	44·58 per cent.
Impurities of crude cresol .	0·76	4·40 ,,
Potassium linoleate . .	19·80	27·83 ,,
Glycerin of soap . .	2·13	3·48 ,,
Glycerin added besides .	...	4·12 ,,
Water	21·34	9·32 ,,
Ashes	6·51	7·17 ,,

Lysol is employed for the same purposes as creoline (or carbolic acid), especially also for surgical operations. They both render the skin and the instruments slippery on washing, which is not the case with the "Cresol Raschig," to be described later on.

According to Rapp (*Chem. Zentr.*, 1909, ii., p. 2206) a sample of lysol, analysed by him, contained 52 per cent. anhydrous cresol, about 30 per cent. fatty acids, and 0·6 per cent. neutral oils. The percentage of *m*-cresol in the lysol-cresols was 43·4 per cent. If in lysol the fatty-oil soap is replaced by linseed-oil soap, with the same percentage of aliphatic acids, the disinfecting-property is much the same; indeed, linseed-oil soap is more suitable than fatty-oil soap; even better is a rosin-soap, *e.g.* made from larch-turpentine. The superior germicide action of lysol in comparison with other cresol soaps is due to the high percentage and the choice of the cresols.

Lysol is applied to the same purposes as creolin and carbolic acid for surgery and disinfecting purposes; but on account of the danger of using it improperly it has been retired from open sale by a decree of the German Federal Council of 1st February 1906, so that it can be obtained only by a doctor's prescription. For the pickling of timber it has never been applied on account of the cost.

Similar Preparations.—Knoll & Co. (Ger. P. 166975), in order to purify heavy tar-oils for therapeutic purposes and prevent their darkening in course of time, first remove the acid oils and bases, then wash them several times with 2 or 3 per cent. concentrated sulphuric acid with the assistance of oxidizing agents, wash again with alkali, and redistil them at diminished pressure in stills where they do not come into contact with base metals.

A product obtained in this way is sold as *Anthrasol; cf.* Bokorny in *Chem. Zeit.*, 1904, p. 990.

Seyd's *Lysokresol* is described by Arnold and Mentzel (*Apoth. Zeit.*, xviii., p. 134; *Chem. Centr.*, 1903, i., 784). They give analyses, quoting the thousandth part of a milligram of cresols and neutral oils. Lysokresol evidently differs from real lysol only by containing more water and being made from impure cresol.

Lysoform is a mixture of lysol and formaldehyde. A similar product is the carbolic-acid soap, described in Rosemann's B. P. 28277, of 1902, which is prepared from crude, water-white cresol, with addition of 2 per cent. formaldehyde and 240 per cent. formaldehyde-potash soap, containing 15 per cent. formaldehyde. It is stated to be almost devoid of smell, easily soluble, not very poisonous, and very efficient.

Lysosuphol (*Pharm. Zeit.*, 1901, p. 93) is a sulphur compound, soluble in water.

Carbol-lysoform is a mixture of 2 parts lysoform and 1 part crude carbolic acid.

Sapophenol (*Pharm. Zeit.*, 1905, p. 249), sold by Dr Wermund & Co., is stated to perform the same functions as lysol.

Boleg (Ger. P. 122451) produces tar-oil emulsions by mixing the tar-oils with *rosin oil*, and washing with steam and caustic-soda solution, separating from the rosin-soap solution, oxidizing with air or ozone, and in the end treating with steam at a plus-pressure of 1 to 1½ atmospheres. A further patent (Ger. P. 129480) prescribes regulating the viscosity of the oils, after being made soluble in water by the addition of 50 to 60 per cent. condensed water, with a little gelatine, and then treating in the oxidation apparatus at a slowly rising temperature (115° to 125° C., according to their specific gravity) with compressed air until the mixture has become perfectly clear. This process is declared by Künkler (*Seifensieder-Zeit.*, 1902, p. 510) to be quite useless.

Westrumite is a preparation, like Boleg's, used for watering public roads.

A further patent of the Boleg Company (Ger. P. 155288; B. P. 22091, 1903) prescribes treating the oils as in Ger. P. 122451, mixing with aromatic hydrocarbons, previously treated with air or ozone at a temperature of 50° to 70° C., with application of compressed air, heating the mixture to a pressure of 1 to 1½ atmospheres in high-pressure boilers, and slowly cooling down.

The very great advantages of tar emulsions over the oils themselves for preserving timber, etc., are forcibly pointed out by Seidenschnur in *Z. angew. Chem.*, 1901, p. 43.

Nördlinger (Ger. P. 168611) makes heavy tar-oils more suitable for impregnating and disinfecting purposes by mixing them with neutral or acid metallic salts of *fatty acids*, beginning from propionic acid, up to caprinic acid, or the analogous salts of the acrylic acid series, or solutions of these salts. These salts are more easily soluble in tar-oils than the acetates, and their antiseptic action is consequently greater, while they are less easily washed out.

The Aktien-Gesellschaft für Teer- und Erdöl-Industric (Fr. P. 309807, 1901) find that the salts of *phenanthrene* mono- and disulphonic acids act as solvents for cresol, and so do the sulphonates of other tar hydrocarbons and of carbazol. The solutions are valuable as disinfectants or for pickling timber.

Spalteholz (Ger. P. 169493) employs for the purpose of preparing the tar-oil emulsions an alkaline solution of *casein*, preferably with an addition of a small quantity of rosin. It is claimed that these emulsions are not destroyed by the salts contained in ordinary water, as is the case with creoline, lysol, etc. The same inventor later on (Ger. P. 170332) recommends for the same purpose preferably the products obtained from casein by treatment with alkalis, acids, or by fermentation, always in an alkaline solution.

The Berliner Holz-Comptoir (Ger. P. 117263) employs a soap-solution of tar-oils "of the well-known kind" for thoroughly impregnating timber, as it penetrates into this right into the centre.

The same firm (Ger. P. 139441) produces a lasting emulsion from tar-oil and zinc-chloride solution, by mixing 5 to 50 per cent. *wood-tar* to the creosote oil, adding the aqueous solution of $ZnCl_2$, and passing air through the mixture for some time at boiling heat.

The same firm (Ger. P. 152179) has found that the desired result is obtained in much shorter time, by first blowing air through the mixture of creosote oil and wood-tar for a short time, and then gradually adding the $ZnCl_2$ solution, always stirring by air. In this case the temperature need be kept only at 60° to 70° C.; the mixture is more durable, and can at once be drawn or forced into the impregnating vessels.

Emulsions of Tar-oils, produced by Sulphuric Acid.—A very much employed process for producing emulsions from heavy tar-oils, consisting of a mixture of actually dissolved compounds with oils in a very fine state of division, is the treatment with concentrated *sulphuric acid* (Artmann's Ger. P. 51515, 1889), by which the alkaline compounds (pyridines, etc.) are converted into salts, the phenols and some of the hydrocarbons into sulphonated derivatives soluble in water, and holding the undissolved oils in a state of suspension which lasts for a long time without any separation from the aqueous portion. According to a private communication from G. Kraemer, the sodium and potassium sulphonate of acenaphthene and phenanthrene are most efficient in forming such emulsions. These emulsions may be entirely fluid or of a more gelatinous kind, and they are, like tar oil emulsions, produced in other ways, employed for pickling timber, as cooling agents in the drilling of iron, for treating textile fabrics, for laying the dust in public roads,[1] and other purposes.

Knoll & Co. (Ger. P. 106500) treat tar with concentrated sulphuric acid at 100°; the reaction products are insoluble in water, but can be converted by alkali into solutions of almost neutral reaction.

Alb. Friedländer (Ger. P. 181288) makes phenol or its substitution products soluble in water by adding small quantities of sulphonic acids or sulphonates.

These processes produce a greasy mixture of sulphonated phenols and hydrocarbons, quinoline sulphate, and insoluble oils, from which on dilution with water or ferrous sulphate solution very disagreeable tarry masses are separated (Kraemer and Spilker, p. 61).

Other patents for tar-oil emulsions have been taken out by van der Ploeg (B. P. 7699, of 1905); F. Saint-Hilaire and E. Grousseau (Fr. P. 353663); Nördlinger (Ger. Ps. 121904 and 168611).

The tar-oil emulsions have lost much of their importance for impregnating timber by the modern economic processes for this purpose, e.g. that of Rüping (p. 686). A drawback to their employment for laying the dust in public roads is the strong smell they possess.

Employment of Creosote Oil as a Lubricant.

This can be efficiently done only after removing the phenols (acids), which promote friction. Naphthalene also will hardly be adapted to promote lubrication. But the mixture of non-solidifying oils, which come before and along with anthracene, is really a lubricant, at least after proper treatment, and this sort of grease is pretty extensively used at collieries, etc., although the heavy paraffin and petroleum oils and rosin oil are far superior lubricants, and are nowadays cheap enough to make the employment of coal-tar oils superfluous.

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[1] According to *Asphalt u. Teerind. Zeit.*, iii. 271, this has been done successfully at Turin, but for this purpose the oil must be free from naphthalene.

In order to prepare the latter for this purpose, the phenols (commonly called "acids") must be removed. This would be done effectually by treatment with caustic soda; but as this is mostly too expensive, the cartgrease manufacturers treat the oils with lime, similarly to rosin oils, with which they are generally mixed. Thenius[1] prescribes gradually adding to a hundredweight of crude rosin oil, contained in a retort, 56 lb. of slaked lime, and heating, with agitation, till the whole is dissolved, then distil for an hour, condensing the vapours. The mass is now allowed to settle and the clear portion is run off. On the other hand, 1½ cwt. of dry slaked lime is mixed in an open pan with ½ cwt. of rosin oil and ½ cwt. of heavy coal-tar oil freed from acids; the mass is stirred and heated till it is quite homogeneous, and is then allowed to cool while being constantly agitated. From each of the two mixtures thus prepared ½ cwt. is taken and mixed up in a pan; and, with constant stirring, a third mixture is added, consisting of 23 lb. of melted ozokerite, ½ cwt. of heavy coal-tar oil free from acids, and ½ cwt. of heavy rosin oil. The latter mixture is added when it has cooled down to some extent, but before it has solidified. It may be coloured yellow with a few pounds of tumeric, or blackish blue by lampblack.

Thenius also describes another kind of cartgrease, made of a mixture of a tallow-soap, fish-oil, potash-soap, and coal-tar-oil.

Dumoulin and Coutelle prepare lubricating oil by stirring up 2 cwt. of creosote oil, 11 gall. of water, 2 lb. of bleaching-powder, 2 lb. of soda-ash, and 1 lb. of manganese, settling twenty-four hours, decanting the clear liquid, distilling it, and mixing the distillate with one-fourth of its weight of rosin oil: this treatment is to remove the "gummy" part of the tar-oils and to make them inodorous. Or else the oil may be distilled before adding the ingredients.

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[1] *Verwerthung des Steinkohlentheers*, p. 82. (This prescription is considered of very doubtful value by competent authorities.)

Employment of Creosote Oil for Lighting.

Creosote oil has long been used as an illuminant during the construction of harbours, railways, etc., where the smoke caused no inconvenience. But this burning in open pans is a most wasteful, crude sort of illumination. The just-mentioned process of Dumoulin and Coutelle was intended to make creosote oil fit for lighting even dwelling-rooms; but that degree of success is very doubtful. In order to get a proper lighting-effect, it is indispensable to introduce a jet of air, which prevents the formation of black smoke and burns the soot. Hence everything depends upon the construction of the *lamps*. One of the best lamps for this purpose is the steam-jet lamp of Hartmann and Lucke,[1] shown in Figs. 150 and 151. The steam-jet serves not merely to convey the oxygen necessary for combustion, but also to decompose the carbon compounds, thus preventing the formation of soot and producing an intense light. This lamp can of course be employed for any cheap petroleum or tar-oils, but is specially intended for ordinary creosote oil; it does not require a mechanical blast, but may be placed wherever steam can be had, and is thus principally adapted for lighting large factory workshops, yards, etc., but not for places which require a less intense and more divided source of light.

In the vessel *a*, filled with oil, is suspended the air-supply pipe *b*, ending at the top in a funnel, *c*, provided with a slide to regulate the supply of air to the vessel *a*. Hence the oil must flow out of *a* quite evenly, on Mariotte's principle, the pressure being constant. It flows through the cock *e* and the pipe *g* into the dish *d* (which must be mounted in a perfectly horizontal position), where it is lighted and then covered with the funnel *f*: as the oil is difficult to light, it is first covered with a little petroleum. Steam, first dried in the apparatus *k* (Fig. 151), is now, very slowly, admitted through the conical opening in the dish *d*. As soon as the oil burns equally all over the dish, which is brought about by regulating the steam-supply, the lamp requires no more attention. If by a wrong position of

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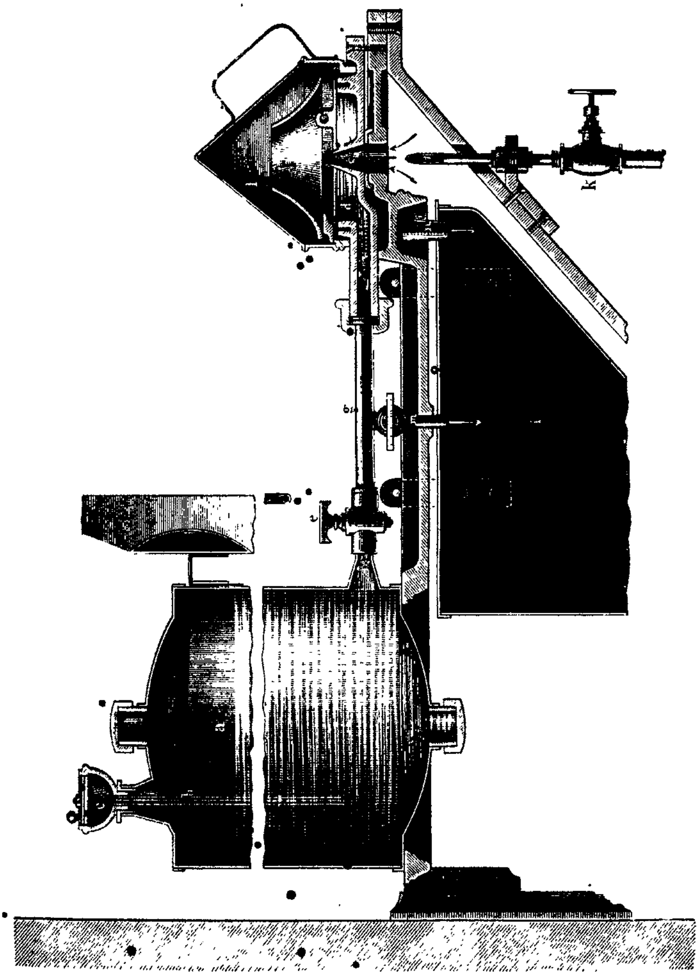
[1] German patent No. 9195, 9th August 1879.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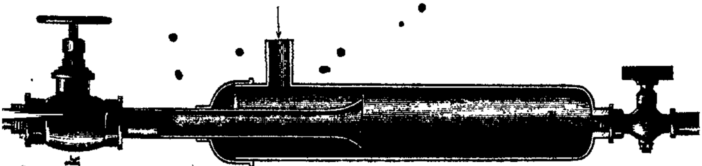
k

the slide at *c* the dish is supplied with more oil than can be burnt, the superfluous portion overflows into the annular channel round the dish and through the tube *h* into the vessel *i*. At first it is best to let it overflow; afterwards, when the oil has become hot, its supply is regulated so that the inner part of the dish always remains full. To put out the lamp, the cock *e* is shut (so that no more oil flows into the dish), the steam is shut off by the cock *k*, and the flame is extinguished by putting on the funnel-shaped cover *l*. The oil remaining in *d* and *g* is run into *i* by opening the tap *m*. This is a threeway-cock, which either conveys the oil to the burner or else discharges it into the vessel *i*.

The steam admitted underneath the dish *d* acts mechanically by forcing the air necessary for combustion into the flame, and also by aspirating the air from without through the openings beneath the funnel *f*. The steam also acts chemically upon the hydrocarbons, forming a gaseous mixture, which, on combustion, produces an extremely brilliant light and no soot. This is not attained by ordinary lamps, because in them, when enough air is admitted, the flame becomes hotter but not more luminous. The steam should be as dry as possible, and the condensed water must be allowed to run away.

Thus the tar-oil burns without wick or chimney, preferably in very large glass lamps with reflectors. Such a lamp gives a light of 20 ordinary gas-lights or 180 standard candles, with an hourly consumption of about 2½ lb. of tar-oil. The oil-vessel holds about 7 gall., so as to suffice for the longest winter nights. The lamps need no cleaning or repairing.

A more recent form of this lamp is shown in Fig. 152, $\frac{1}{12}$ natural size; this shape costs £5 including package, the glass lamp £4. Where the carriage does not make the oil too dear, this light is much cheaper than gas-light.

Another apparatus for the same purpose has been patented by Messrs Lyle & Hannay (67 Great Clyde Street, Glasgow), under the name of the "*Lucigen*." I owe the description of it to the kindness of Mr S. B. Boulton. It consists of an oil-tank or reservoir (Fig. 153, p. 670), fitted with a special burner at the top of a tube, H, which can be made to any length. Into this reservoir compressed air is introduced by an india-rubber pipe, this material being used to make the "Lucigen" portable. On the compressed air being let into the tank at A (B is a moisture-trap, C a blow-off cock), it forces the oil up through an internal tube, and, escaping at the same time through D, O, and E, with the oil in the burner J and combustion chamber L, produces a spray which is set on fire. M is a wind-guard, K and N regulating jam-nuts, G a safety-valve. The pressure at which the air is forced into the accumulator is about 15 lb.; and

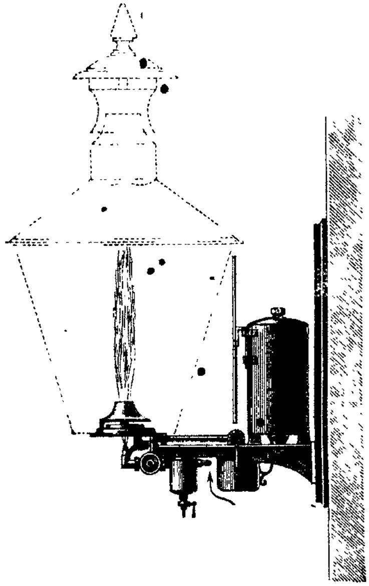

FIG. 152.

this is sufficient to supply the whole of the lights. A light of about 2000 candle-power is given by the "Lucigen." The flame is large, and the light well-diffused, and the eyes are not dazzled by it. It is claimed by the patentees that the "Lucigen" is much more distributive in quality than the electric light, and that it does not cast such deep shadows; also that it is much cheaper, alike in cost and maintenance, than either gas or electric light. It can be produced by either air or steam at a nominal expenditure of power, and it does not require any neat adjustment of machinery. The oil used in the Lucigen is the refuse of chemical- and gas-works, and about 1 gall. per hour is consumed. Owing to the application of pressure, the "Lucigen,"

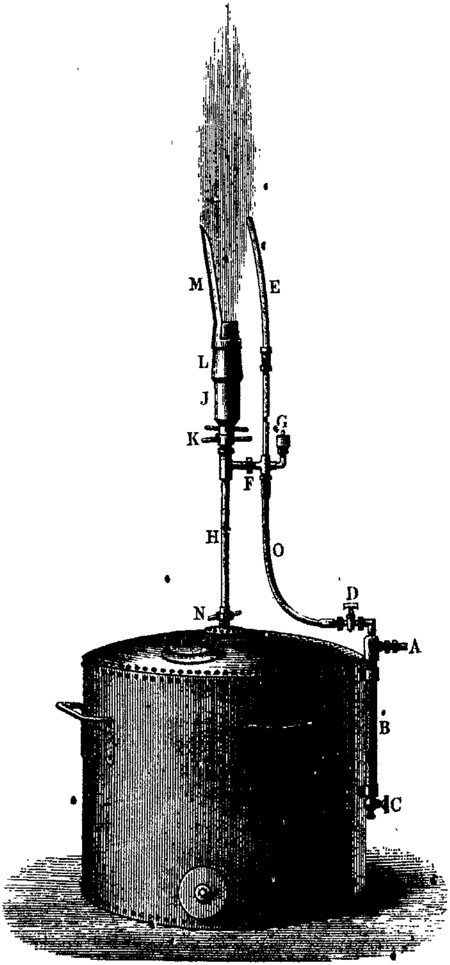

FIG. 153.

when burning, emits a sound resembling steam blowing off. This, in a confined building, would naturally be very disagreeable; but in the open air the hissing noise emitted is not very annoying. There is scarcely any smoke from the light; and the smell of the consumed oil is not offensive. The Lucigen burns equally well under heavy rain or spray. It does not need any lantern, and has no parts which can be damaged by rough usage.

An improvement upon the Lucigen light is Grube's "Oleo-vapour lamp," shown Fig. 154. The reservoir is filled by a pump, M. to three-fourths of its capacity with creosote oil, the air above the oil being compressed, as shown by a pressure-gauge. Thus the oil is forced into the burner R, which, after being once heated up, automatically heats and vaporizes the oil. For this preliminary heating, which takes eight or ten minutes, some oily cotton-waste is burned on the plate C. Once the flame has formed, the vaporization is effected by it. The flame gives a fine, bright light, not so glaring as arc-light, without any soot; it consumes 6 litres of creosote oil per hour, and requires no attention except pumping the oil every two hours. Such lamps are made of from 1000 to 5000 candle-power.

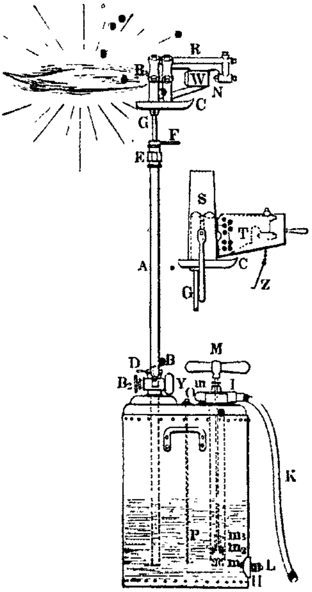

FIG. 154.

A similar apparatus is Luther and Rose's "Portable Sunlight," described in the *Chem. Trade. J.*, 1887, p. 202. A steel cylinder, tested for 9 atmospheres' pressure and provided with a safety-valve, holds the oil; it is surrounded by a cast-iron jacket. The oil is vaporized by means of a small coke-fire, and is passed into the combustion-chamber, where air is introduced, without a blast or the like, in such quantity that the oil-vapour, issuing under a pressure of 3½ atmospheres, is burned completely with a dazzling white light. The patentees manufacture lamps up to 3000 candle-power, and they state the cost = 1d. per hour for 1000 candles (?).

The employment of creosote oil for *carburetting gas* will be discussed later on, along with that of other tar-oils (Chapter XI.).

Application of Creosote Oil as Fuel.

On pp. 422 *et seq.* we have discussed the application of coal-tar for heating purposes. Most of the processes and apparatus described there can also serve for burning creosote oil as fuel—an application of that oil which has during recent years more and more increased. At tar-distilling works it has always been usual to use any oils which for the time being are unsaleable for that purpose, both for heating the tar-stills and for the steam-boilers. But only during the last twenty years these oils have found an extensive application as fuel in other ways, *e.g.*, for heating the boilers of steamers, for glass-works, and for metallurgical purposes. This application is certainly partially due to the extraordinary advantages connected with the use of tar-oils as fuel; the greatest impetus has been given to it by the over-production of such oils, as well as that of the tar itself (*cf.* Pick, *Heizöl oder Kohle*, Vienna, 1909, pp. 5 *et seq.*). This, indeed, has generally led to the construction of industrial fireplaces to be supplied with liquid fuel. This proceeding originated during the last century in England, in which country the rapid extension of gas-lighting led to the production of large quantities of coal-tar, far in excess of the demand. This state of matters changed, of course, when a constantly increasing demand for coal-tar products took place in the industry of aniline colours, as well as for the purpose of impregnating timber, and for the manufacture of patent-fuel. In 1864, Audouin and St Claire Deville, at the request of the Emperor

Napoleon III., experimented on the application of the heavy coal-tar oils for the production of steam. They obtained very satisfactory results in that way, which, however, could not be carried out on an industrial scale, owing to high prices of those oils prevailing at that time (cf. *supra*). The recent enormous extension of the processes of converting coal into coke with recovery of the by-products, especially in Germany, has caused a corresponding application of tar-oils as fuel for steam-boilers and other purposes.

The industrial application of liquid fuel for various purposes has principally been developed in connection with petroleum. One of the first steps in this direction was a patent, granted to Bidle, Shaw & Linton, in 1862, for applying this method to steam boilers. In Russia Spakowski, in 1866, constructed the first burner for liquid fuel for steam-boat boilers; nowadays all the steamers on the Caspian, and all the locomotive engines on the railways in that district, are worked in this way.

One of the principal reasons for preferring liquid to solid fuel is the great heating-value of the former. H. Ste. Claire Deville found the heating-value of the heavy tar-oils of the Paris gas-works (sp. gr. 1·044, containing 82·00 per cent. carbon, 7·60 per cent. hydrogen, and 10·40 per cent. oxygen) = 8916 metrical calories per 1 kg. Rieppel (*Z. Verein. deutsch. Ingen.*, 1907, p. 613) states the average heating-value of coal-tar oils per kg. = 8999 calories (that of lignite oils = 9720 calories, of petroleum and the oils obtained from it = 9908 calories). Veith (*Das Erdöl*, 1842, p. 440) reports on comparative trials, made under equal conditions with the same steam-boilers, in which 1 kg. of coal evaporated on the average 7 kg. of water, and 1 kg. petroleum 13·5 kg. water. Piek (*loc. cit.*, p. 51) gives the results obtained by various observers, showing the evaporating-power for 1 kg. as follows (in litres):—

	Minimum.	Average.	Maximum.
American coal . .	6·41	8·27	9·64
English ,, . .	6·24	7·82	9·15
Prussian ,, . .	6·98	8·28	9·18
Saxon ,, . .	8·04	8·20	8·30
Crude petroleum . .	12·00	13·00	14·50
Heavy coal-tar oils .	10·50	12·00	13·00

Very extensive experiments on the application of coal-tar oils for raising steam were made in the months from February to August 1910, at the request of the Deutsche Teerprodukten Vereinigung, in the laboratory of the Technical University at Charlottenburg, by Professor Josse, with the assistance of Mr Hanszel, with a steam-boiler, fitted with two internal heating-tubes. They found the average evaporating-power of coal of ordinary quality = 6.5 kg. of water, that of coal-tar = 11·7 kg., and taking regard of the saving of manual labour, etc., etc., they declare that the value of the tar-oils for steam-receiving is *at least* twice as high as that of coal.

The superior heating-value of all kinds of liquid fuel in comparison with coal is, in the first instance, caused by its chemical composition, but moreover by the fact that it can be burned with little more than the theoretical quantity of oxygen (air), without losses caused by incomplete combustion (soot) and by combustible substance remaining behind. A further advantage is that the flame of the oil can be at any moment lighted or extinguished. The heating-up of the steam-boilers takes place in half the time required with coal. Since there is no human labour required for getting the fuel to the boiler, charging it on to the grate, removing the soot and ashes, etc., there is an enormous saving of labour. One fireman can easily look after ten to fifteen fires. No elevators, mechanical grates, etc., are required. There is a saving of from 40 to 50 per cent. space for the oil, against that of the coal-bunkers, and the oil-tanks need not, like the coal-bunkers, be placed close to the fires, but at any convenient place. At the World's Fair at Chicago there were 52 steam-boilers heated by petroleum, producing 52,000 horse-power, served by two men and a superintendent. 'The only drawback of liquid fuel is that some descriptions of it at lower temperatures become pasty; but in the case of coal-tar oils this can be avoided by the previous removal of naphthalene, anthracene, etc., and by keeping the store-tanks and pipes warm by means of exhaust-steam.

In countries possessing no considerable stocks of petroleum, but a highly developed coal-tar industry, like Great Britain and Germany, the tar-oils fill up the gap. Great Britain produces upwards of a million tons coal-tar, to which must be added about 65,000 tons of oils, suitable as fuel, from the Scotch shale, so that about 450,000 to 500,000 tons of fuel-oils are at disposal, from which certainly the amount consumed for pickling timber must be deducted. In Germany from more than 1,000,000 tons of coal-tar about 350,000 tons of tar-oils are obtained; and about 50,000 of fuel-oil from lignite-works and 80,000 tons petroleum, bringing up the quantity of oils disposable as fuel to upwards of 400,000 tons. And these figures are increasing every year!

In a former chapter (pp. 338 *et seq.*) we have described the apparatus employed for converting coal-tar into a *spray*, for the purpose of producing heat by its combustion. Similar apparatus can serve for creosote oil, or waste oil from working up other fractions of coal-tar distillation. The combustion of these oil sprays is practically a case of gas-firing; for this spray is immediately converted into gases and vapours by the radiant heat of the fireplace—much more than tar when used in the same manner, for there is not, as is the case when burning tar, a secretion of free carbon and of bituminous substances. Altogether these oils are a much better fuel than raw tar. The latter cannot be employed for locomotive boilers, whilst the oils are used for this purpose to a considerable extent, *e.g.*, on the Prussian State railways. According to Sussmann (*J. Gasbeleucht.*, 1910, p. 477) the employment of tar-oils as sole fuel for locomotive engines had been given up again, but the oils had been most successfully employed in connection with coal fires, enabling the locomotives to do much more work than when they are heated by coal or coke fires, and greatly reducing the strain upon the firemen. Quite recently attempts have been again made to use the tar-oils by themselves, especially on lines going upwards with a steep slope and with restricted traffic. According to Pietrusky (*Z. angew. Chem.*, 1905, p. 343) the first tank-steamer in which tar-oils are the only fuel was put into duty in 1904 by the German War Office, in order to make the men-of-war independent of the stores of fuel on land.

The spraying of tar-oils (for which, apart from the spray-producers described *supra*, p. 338, special apparatus has been described by Rispler (*Chem. Zeit.*, 1904, p. 157) and M'Murtrie (Ger. P. 163164)) in the case of steam-boilers, distilling-apparatus, evaporating-vessels, and altogether wherever the contents of a vessel are heated *from without*, is mostly produced by means of steam, less frequently by compressed air. When using steam, this at the same time draws in the air required for burning the oil, and brings it into intimate contact with gaseous or vaporized fuel. Possibly the steam itself takes part in the burning-process, in so far as its oxygen combines with the carbonaceous products, with liberation of hydrogen; but, of course, there is no question of the heating effect being thereby increased.

The spraying of the oil by means of steam is excluded in the case of metallurgical processes, in glass-making, etc. It must be effected in these cases by compressed air, in the first instance because when employing steam the temperature produced is not sufficiently high (according to Josse it is 1300°, against 1600° when spraying by compressed air); moreover, according to Goulischambaroff, because the free oxygen produced by the splitting-up of aqueous vapour, even in the presence of hydrogen, produces a superficial oxidation of metals, preventing their fusing.

The application of oil-firing in smelting metals, etc., has been first made in America, where the oil at disposal was in the shape of petroleum residues or "Texas oil." In that country there is an enormous number of crucible furnaces heated in this way. Recently several European firms, especially in Great Britain and Germany, have entered into this field, constructing their plant for utilizing also coal-tar oils as fuel. We shall mention some of these constructions, comparing the work done therewith with that which is done by coke fires, as reported by Teichmann and Bross, in *Stahl u. Eisen*, 1911, pp. 843 and 1049.

For fusing Metal in Crucibles.—The consumption of tar-oils is generally stated at 10 per cent. against 14 to 24 per cent. coke. The cost of the fuel is, at present prices, practically the same in both cases, but the other advantages of liquid fuel (*vide supra*, p. 673) have recently caused several large firms to introduce oil-fired furnaces for all new plant, and for replacing worn-out crucible furnaces.

C. Männel, of Hanover-Vahrenwald, supplies oil-furnaces, on the system of Buess, for charges of 75, 150, 300, and 500 kg. These furnaces, which have had a full success, consist of a cylindrical iron vessel, lined with fireclay, suspended by two pins, and turning on these by means of a cog-wheel. In the inside space of the cylinder the fusing crucible is placed on a fireclay support. The tuyere, passing through one of the hollow pins, receives the oil by natural fall, and air preheated to 100° to 200° for producing the spray, at a pressure of 0·8 atmos. More hot air is blown in and produces a white, perfectly smokeless flame, which surrounds the crucible and comes out through the top cover; it is still further utilized for pre-heating the metal and crucible for a fresh charge. The time required for fusing the metal varies from thirty to forty minutes, according to the weight of the charge. The consumption of fuel varies from 8 to 10 kg. tar-oil of medium quality per 100 kg. metal. The crucible always remains in its place, and lasts for fifty operations and upwards. These furnaces have been widely introduced in German foundries for bronze, grey metal, and precious metals.

Other descriptions of oil-fired crucible furnaces, *e.g.*, those constructed according to a patent of Helbig, have also been widely applied in Germany.

For melting large charges of metal and for glass-making, oil-fired furnaces dispensing with a crucible have been introduced, principally in America, *e.g.*, the Schwarz furnace (*Z. f. prakt. Maschinenban*, 1910, p. 1781). Here the oil is blown in at the top through a tuyere, and the flame strikes the metal directly. These furnaces are built up to a capacity of 8 tons of metal.

For the *chlorinating-roasting* of metallic sulphides, according to Pietruski (*Z. angew. Chem.*, 1905, p. 343), tar-oil fired furnaces have proved a great success. The process lasts only forty minutes, against two and a half to three and a half hours by ordinary fires.

Tar-oil furnaces have also been widely introduced for metallurgical furnaces of various descriptions, for hardening, welding, enamelling, etc., going up to a temperature of 1800°, and easy to regulate. In the "Calorex" and "Empire" furnaces of Gebrüder Boye in Berlin (*Ger. Musterschutz*, 283543 and 366951) there is a saving of 60 per cent. against heating by coal-gas. Rockwell & Co. at New York build continuously and automatically acting furnaces, of a duty of 250, 500, and 750 kg., with a consumption of 15, 20, and 30 kg. (respectively) of fuel-oil.

Irinyi (Ger. P. applied for) has constructed a tar-oil burner, working without steam or compressed air, which serves equally well for domestic fireplaces and for the largest steam-boilers, dispensing valves, floats, and other easily damaged parts. Koehler (Lunge and Koehler's *Steinkohlenteer und Ammoniak*, 1912, i., p. 680) convinced himself of the excellent working of Irinyi's burner which for heating a room of 100 cb.m. required 400 to 500 g. tar-oil per hour.

The application of tar-oil firing to a Siemens-Martin furnace by the R. Wolff Aktien-Gesellschaft at Magdeburg-Buckau, in lieu of producer-gas, according to *Stahl u. Eisen*, 1914, p. 1424, has been very successful.

Application of Creosote Oil as Fuel in Explosion Motors and Caloric-motor Engines.

Explosion motors, worked by oils boiling only at high temperatures, were first constructed in 1897 by Diesel, by means of very high compression, fusing crude naphtha, masud, paraffin oil, etc. The attempts at employing heavy tar-oils for this purpose were at first unsuccessful, as reported by Müller (*Petroleum*, 1910, p. 356), Kutzbach (*Z. Verein. deutsch. Ingen.*, 1907, p. 521), and Rieppel (*ibid.*, p. 613). This task was finally solved by mixing the creosote oil with from 3 to 5 per cent. easily inflammable oil, for which purpose oven tar-oils of lower boiling-points (150° to 180°) can be employed. Diesel motors working in this way are built by the Gasmotorenfabrik Deutz and by the Maschinenfabrik Augsburg-Nürnberg, and employed especially in Germany and Russia.

British patents for the use of creosote oil in explosion motors have been taken out by Boswell (B. P. 22853, of 1904), and by Albone and Boswell (B. P. 24449, of 1904).

A comprehensive paper on the application of creosote oil for heating and motoric purposes was read by Hausenfelder on 14th January 1912 (*Stahl u. Eisen*, 1912, p. 772).

Application of Creosote Oil for Pickling Timber.

This has become an industry of great importance, more especially for railway sleepers, telegraph poles, and piles used for harbour piers. Most of the oils distilled from coal-tar is employed for this purpose, and we can trace the first development of tar-distilling to the demand which arose for such oils consequent upon the introduction of Bethell's process (1838).

The history of timber-preserving in general, and that of the "creosoting" process in particular, has been given in several publications, of which especially that by Mr S. B. Boulton ("On the Antiseptic Treatment of Timber," *Proc. Inst. Civ. Eng.*, 1883-84, vol. lxxviii., pp. 4 *et seq.*) contains much original matter; this subject is also treated by Adolf Mayer's *Chemische Technologie des Holzes* (Braunschweig, 1872), Buresch's *Der Schutz des Holzes* (2nd ed., Dresden, 1880), and Heinzerling's *Die Conservirung des Holzes* (Halle, 1882). To those treatises we refer for a description of the technical part of creosoting which does not come within our domain, and for more detailed statements regarding this subject in general.

Tar and pitch were used for painting or smearing wood in the remotest antiquity; special instances of preserving timber from decay are related in connection with the platform on which stood that wonder of the world, the statue of Zeus by Phidias, at Olympia, and with the famous wooden statue of Diana at Ephesus (Boulton, p. 5). The preservation of the Egyptian mummies may to a great extent be placed in the same category. But we must take a wide step in history before we meet with any widespread application of antiseptics for wood. Apart from a few isolated trials with various antiseptics made during the eighteenth century, we find practically nothing done in this line till the beginning of the present century, although the records of the British Patent Office contain lists of almost every conceivable antiseptic from the year 1768 (Boulton, p. 8). But it is since the birth and growth of the railway system that the antiseptic treatment of timber has received its most important development. By the year 1838 the four systems of timber-preserving which alone are now employed were fairly before the public, and competing for the favour of engineers, namely:—(1) Corrosive sublimate known since 1705, again introduced by J. H. Kyan; (2) sulphate of copper, known since 1767, principally introduced by Boucherie; (3) chloride of zinc, known since 1815, patented again by Sir William Burnett; and, lastly, (4) heavy oil of tar, afterwards called creosote oil, patented by John Bethell.

We shall, of course, occupy ourselves only with the last-mentioned process, which, moreover, has far outstripped the other three in importance, and in England has entirely extinguished its rivals. Vegetable tars, or extracts from the same, were used for timber-preserving, both in England and America, as early as 1756 (Boulton, p. 10). The first to mention the products of the distillation of gas-tar for impregnating timber was Franz Moll (B. P. 6983, January 1836). He proposed to employ, at the commencement of the operation, the oils lighter than water, which he called "Eupion," and afterwards the heavier oils, which he called "Kreosot." Both names were taken from Reichenbach's investigation of the products obtainable from wood-tar, as it was not known at that time what fundamental difference exists in the composition of wood-tar and coal-tar. Real creosote in Reichenbach's sense, does not occur in coal-tar; but the phenol contained in the latter was for a long time confounded with Reichenbach's creosote. Moll's process, so far as the application of light oil was concerned, was manifestly unpractical; but the stimulus was now given for employing the products from coal-tar in that line, and in 1838 followed the practical introduction of the process by Mr John Bethell. The terms "creosote" and "creosoting," now generally used in this connection, are due to Franz Moll; they do not occur in Bethell's patent, which contains a list of no less than eighteen various substances, mixtures or solutions, oleaginous, bituminous, and of metallic salts. Amongst them is a mixture consisting of coal-tar, thinned with from one-third to one-half of its quantity of dead oil distilled from coal-tar; and as late as 1849 Bethell's licenses mention the admixture of gas-tar. In those times inspectors frequently refused to allow the dead oils to be used without being thickened with tar (Boulton, p. 14), as it was not understood that the pitch was only an impediment to the injection. This must have been recognized very soon after. The dead oils came into use alone; and there crept into the specifications the contradictory prescription that the wood was to be creosoted according to Bethell's patent, but that the creosote was to be free from adulteration with coal-tar.

Coal-tar creosote has been recognized as superior to lignite oils, rosin oil, etc., because it contains not merely phenols, like these, but also basic substances which with the phenols and unsaturated hydrocarbons form resin-like combinations, filling up the cells and protecting them from destruction. Some German railway companies positively forbid the employment of creosote oil, containing upwards of 25 per cent. lignite oils for pickling their sleepers.

The *apparatus* now universally employed for impregnating timber, both with creosote oil and chloride of zinc, was first introduced by Bréant, director of the Paris Mint, in 1831, who employed it for injecting linseed oil and rosin. The principle of Bréant's process was adopted by J. Bethell, and greatly improved by himself and H. P. Burt.. Their apparatus, as constructed above seventy years ago, has been adopted everywhere in all its essential features, and is minutely described in the above-mentioned treatises; it is still used everywhere for the above-named purpose, and has been improved in details. It consists of a very strong, horizontal, wrought-iron boiler, 6 or 7 ft. in diameter, 30 to 60 ft. long, and ⅜ in. thick. The timber is placed on iron bogie-frames, which are run upon rails into the cylinder, whose front is then firmly closed by a cover. The air is now exhausted till the air-gauge indicates about ⅛ or ⅛ of an atmosphere; communication is now opened by a cock with a tank holding the creosote oil, heated to a temperature of about 100°, at which it should be perfectly fluid. The oil at once rushes into the vacuum and deeply penetrates into the pores of the wood, whilst at ordinary pressures the air contained in the pores would pertinaciously resist the entrance of the oil. When no more oil is sucked up, a force-pump is started, which presses more oil into the cylinder, till a pressure of 8 or 10 atmospheres has been attained. This is kept up for several hours; and the wood in this operation absorbs on an average nearly a gallon per cubic foot.

The plan of injecting creosote oils or similar substances in a state of vapour, which has been several times tried (Lukin, 1812; Franz Moll, 1836; Bethell, 1864, etc.), could not possibly answer. Timber is weakened by exposure to a temperature much exceeding 120°, and is seriously injured at 150°; but the boiling-point of creosote oils ranges from 200° to about 370°. Hence its vapours can only be injected into wood under such conditions of temperature and pressure as will destroy the value of the timber; and experience has proved this to be the case. Nor has the application of superheated steam, passed through creosote oils, met with much more success (Boulton, pp. 30, 31, and below).

One difficulty of the creosoting process is the *presence of moisture* in the timber to be preserved. In the fresh-cut state, or as it is taken from the timber-ponds, it is not in a fit condition for creosoting, and must be stacked first from four to six months. Many methods have been tried for artificially drying the timber, in order to do away with the necessity of long stacking, which is extremely cumbersome or even impossible when piles, etc., have to be sawn from larger logs, for immediate use in harbour-works, etc.; but they have all been abandoned, as, if the heat applied is really efficient in expelling the water, the woody fibre is sure to be injured in the process. Vohl[1] made a proposal which, if it were successful, would obviate the difficulty, by converting the creosote from an oily into an aqueous fluid; namely, adding enough solution of caustic soda to the creosote to make it miscible with water, impregnating the timber with this liquid, and ultimately "fixing" the creosote with a dilute solution of ferrous sulphate. But as this process was evidently never carried out on a manufacturing scale, nothing further can be stated respecting it.

Another way out of the difficulty is to apply the creosote oil in a heated state, so that the water contained in the timber evaporates during the operation. A process founded upon this principle, but evidently imperfect in other respects, was invented by Pelton, and, according to a report made by Ott in 1874,[2] seems to have been largely employed in America at that period. It consisted in placing the timber, in the green state, in iron cylinders, covering it up with creosote oil and heating this for some time up to 100° or 110°, until the water was evaporated, and running in fresh cold oil. This causes the hot oil, already contained in the cylinder, to penetrate into the pores of the wood, a partial vacuum being formed by the cooling. The apparatus is figured and described in detail in the report quoted.

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[1] *Dingl. polyt. J.*, cxvii., p. 448.

[2] *Wagner's Jahresber.*, 1874, p. 959.

It is very doubtful whether in this way the impregnation will be thorough; the very imperfect vacuum, and the absence of pressure at the finish, make this very unlikely. Pelton's process does not seem to have been very successful, for, according to a communication from Mr S. B. Boulton, a committee of the American Society of Civil Engineers, in the report on the preservation of timber, presented and accepted at the Annual Meeting on the 25th June 1885, does not even mention Pelton's method among the many different processes described.

The object in quest, however, is completely attained by S. B. Boulton's process (B. P. 1854, of 1879). The timber is placed in the ordinary high-pressure creosoting cylinder (A, Fig. 155), which is provided with a somewhat high dome, *a*. After the air has been exhausted in the usual way, the creosote is introduced through the pipe *b* at a temperature a little above 100°; but it is not allowed to rise quite to the top, so that the dome *a* is always kept empty, and the creosote is not drawn through the exhaust-pipe. The boiler B serves for heating up the creosote. The exhausting process is continued, by means of the pump C, until

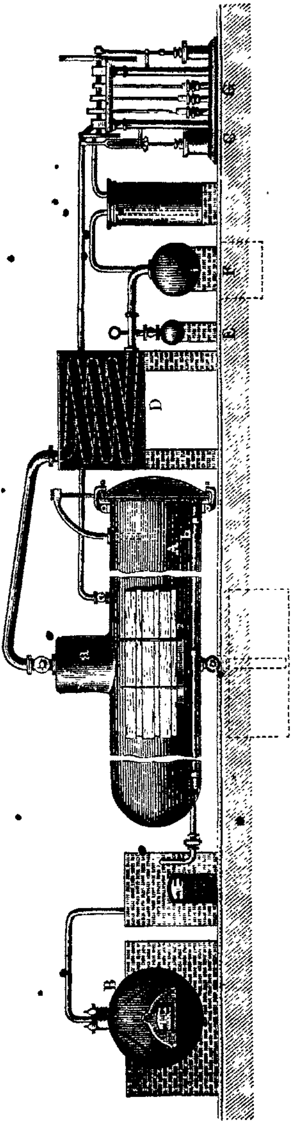

FIG. 155.

all the moisture contained in the pores of the timber has been vaporized by the heat of the creosote oil, and has been drawn away in the state of vapour by the air-pump. As the temperature employed is much below the boiling-point of creosote, this liquid is not turned into vapour. The aqueous vapour is drawn through the dome *a*, is condensed by passing through the worm D, and the water is collected in the receiving-tanks E, F, where the quantity extracted can be measured. The timber may be introduced quite wet; the water it contains is replaced by creosote, as much as 50 gall. per truck-load of timber, say 1½ tons, without ever subjecting the wood to dry heat. The process of injection can then be completed by means of the pressure-pumps G in the usual manner. That is, when no more oil is drawn in by suction, more oil is injected by means of a force-pump until a pressure of from 8 to 10 atmospheres has been reached, which is continued for several hours. According to the rule enacted by the administration of the Prussian State Railways, a sleeper of a length of 2·70 m., holding about 0·11 cb.m., should contain at least 36 kg. tar-oil.

Boulton's process, if applied to very moist timber, involves some additional cost and a few more hours, but not so much time and money as is required for stoving the timber, apart from the risk of deterioration incurred thereby; while for drying by stacking the timber for six months, the interest and the value of the place occupied must be set off against the cost of the new process.

A process patented by Blythe, of Bordeaux (Ger. P. 10423), essentially consists of injecting superheated steam into creosote oil, and allowing the mixed vapours of steam and creosote oil to act upon the wood contained in a closed boiler. The process has been extensively used in France, but with very unsatisfactory results.[1] A sleeper, which, according to the process usually followed in Germany, would take up 18 kg. of creosote oil, absorbs only 11 kg. in Blythe's process.

The Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft (Ger. Ps. 189232 and 195878) performs the impregnation of timber by means of the vapours evolved in the coking of coal.

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[1] *Cf.* Claus, *Wagner-Fischer's Jahresber. d. chem. Techn.*, 1883, p. 1202, where many interesting details are given concerning the results of different methods of pickling timber.

A proposal has been made by Behrens (Ger. P. appl. B48862) to employ the tar-oil after *diluting it with volatile substances*, viz., benzol or petroleum spirit, and recovering the diluents by steaming the pickled timber; but this process has not turned out well, and moreover involves a considerable risk of inflammation, wherefore it has been abandoned. No more successful have been the attempts at introducing the tar-oil into the timber in the shape of an *aqueous emulsion* (Ger. Ps. 53691, 117263, 121167, 139441, 148794, 151020, and 152179).

Attempts have been made to treat the timber by tar-oils *in the state of vapour*, but they have failed because the oils only volatilize at temperatures upwards of 250° or 300°, which is more than the timber can be exposed to, and because, moreover, the tar vapours condensed to liquids in the upper layers of the wood.

We shall now describe the process of creosoting timber, as carried out during many years in the various large establishments of Jul. Rütgers.—The sleepers are exposed in stoves to a temperature gradually raised to 130° C., and are thus treated for at least four hours, until no more aqueous vapour is given off and the sleepers are uniformly heated. The sleepers are introduced while hot, being left on the same bogie, into the creosoting cylinder. After this has been closed air-tight, a vacuum at least as low as 55 mm. (=2 in.) mercury is produced within thirty minutes, and is kept up during another thirty minutes. The cylinder is now placed into communication with the tank holding the warmed-up creosote oil, and, after being filled with it, is brought under a pressure of at least 6¾ atmospheres for upwards of one hour. Beech-wood sleepers should be either stove-dried or steamed in as fresh a state as possible, before the sap has begun to ferment. Stoving is difficult, because beech-wood has a tendency to split; it is therefore preferable to steam the timber till the temperature exceeds 100° even in the interior, and to remove the sap during the same process by lixiviation. When the pickling is to be performed by aqueous solutions, the steamed sleepers are best submitted directly to the impregnating process; but in the case of tar-oils, the timber must be first air-dried, which in spring or summer takes two or three months. Well-prepared and properly impregnated beech-wood sleepers do not suffer in comparison with those made of any other description of wood. The wood is impregnated all through; it remains hard and tough; and the bolts hold quite fast in it, as has been proved many times with rails which had been in use for a long time.

Many attempts have been made to obtain a complete saturation of the wood by comparatively small quantities of tar-oil. Heise (Ger. Ps. 154901 and 174678) and Guido Rütgers (Ger. P. 186530) tried to produce this result by saturating in the first instance the outer layers of the wood with the total quantity of oil, and causing this to penetrate into the inner layers, so as to attain a uniform impregnation, by means of hot water, steam, or hot high-pressure gases. The process of employing hot gases under high pressure (styled in America the "creo-air process," for which Julius Rütgers obtained a U.S. patent) made it possible to confine the quantity of oil, taken up by a standard sleeper, to an average of 7 kg., against 36 kg. taken up by the old process, but the conservation of the wood is not quite as good as by the old process of filling up all the pores with oil.

In the modern *evacuating processes* larger quantities of tar-oil than are to remain permanently in the timber are forced into it by means of high-pressure pumps, and the excess of oil is subsequently removed by the action of a vacuum. This process, which is based exclusively on the expansion of the air contained in the pores of the wood, necessitates the renunciation of driving the oil into all the pores. This drawback is avoided by the process of "hollow impregnation," worked out by M. Rüping, and protected by the Ger. P. 138933, taken out in the name of C. Wassermann. It is nowadays widely applied, and its advantages are recognized by the public bodies concerned. Whilst by the old process 1 cb.m. of pine-wood requires about 325 kg. of tar-oil, the Rüping process allows of attaining a thorough impregnation with only 50 to 60 kg. tar-oil, since only the cell-walls take up the oil, the inner space of the cells remaining empty. In the Rüping process (which has been introduced into many of the establishments belonging to the Rütgerswerke Aktien-Gesellschaft) the timber is taken in its ordinary, air-dried state, and before impregnation saturated with compressed air at pressures varying according to the quality of the wood, but never exceeding 4 atmospheres, the same pressure being maintained in the impregnating cylinder and in the store-basin for the tar-oil, placed at a higher level. This oil is heated to 95°, and on opening a valve runs by the force of gravity into the pickling-cylinder, placed at a lower level, until that cylinder is quite filled, the oil forcing the air from this cylinder into the tar-reservoir, and completely surrounding the timber. At this stage the timber is on the outside completely surrounded by tar-oil, but the cells and other hollow spaces are filled with compressed air, which at this stage prevents the oil from penetrating into the wood. Now the tar valves are closed, and the pressure is increased to 7 atmospheres. At the same time more tar-oil is forced into the pickling-cylinder, and completely soaks into all impregnable parts of the timber; the air contained in the cells is still further compressed, and forced into the inner spaces of the wood. As soon as the wood has taken up a sufficient amount of tar-oil, the pressure is released, whereupon the compressed air contained in the cells expands and throws out the oil not soaked up by the cell-walls, which then goes back into the store-basin. The principal action of this process is: that more tar-oil is forced into the wood than this can ultimately retain, and that hence the wood becomes thoroughly soaked. In order to facilitate the expulsion of the excess of tar-oil, the wood is exposed to a vacuum for some time. The amount of pressure of the air and the liquid, as well as the temperature of the oil and the time during which the pressure is maintained, are regulated according to the quality of the wood and the amount of moisture contained in it.

Scientific investigations on the conserving action of tar-oils (Seidenschnur, *vide* p. 690) have shown that wood containing in its permeable parts only 7·5 kg. tar-oil per cubic metre resists all the attacks of micro-organisms for many years. Since in the Rüping process the pine-wood takes up from 50 to 60 kg. tar-oil per cubic metre, there is a seven- to eight-fold security produced.

According to Schneidt (*vide infra*) the Rüping process in the year 1909 was in use in various countries by forty wood-impregnating works, in which nearly 4 million cubic metres of wood were treated by it, most of it in Germany and the United States.

Chaligny and Guyot-Sionnest have constructed a *travelling apparatus for pickling timber*, mounted upon two railway trucks, which enables the pickling operation to be performed at every railway station (Armengaud's *Publication Industrielle*, 1884-85, vol. xxx., p. 295; *Dingl. polyt. J.*, vol. cclx., p. 75). Such apparatus, of their own construction, is also employed by Messrs Burt, Boulton, & Haywood in their French establishment.

Drittler (Ger. P. 75805) employs an apparatus for simultaneously exhausting the air and forcing in the pickling liquid. R. Schulz (Ger. P. 53854) and Liebau (Ger. Ps. 50295 and 52893) try to avoid the necessity of pickling at special works by applying a small apparatus for that purpose to the felled trees themselves.

Altena (B. P. 15631, 1906; Ger. P. 175691) places the wood in trucks which are run on to a stage near the top of a vessel resembling a gas-holder. This vessel can be raised or lowered above a reservoir containing the impregnating liquid, by admitting or withdrawing compressed air from it. When it is in its lowest position, the charge of wood is completely covered by the liquid. Air is then quickly admitted so as to raise the vessel, and, at the same time, to force the liquid into the wood, the operation being repeated if necessary. Special means of regulation are supplied to guard against too rapid an ascent or descent of the vessel.

D. de Nagy (B. P. 12427 of 1913) in carbonizing timber, soft coal, lignite, shale, and peat in piles without retorts or ovens, arranges chambers beneath for creosoting timber by means of the distillation products.

Many other apparatus have been patented for pickling timber, into which we cannot enter here.

Special Treatment of Creosote Oils for their Application to the Conservation of Woods.—M. Frank (Ger. P. 139843) digests coal-tar with 10 per cent. of brimstone up to the point where the evolution of hydrogen sulphide ceases. This treatment, according to him, imparts to the oils a remarkable conserving property, especially if they have been previously deprived of the acid constituents (phenols), and therefore consist entirely of neutral oils.

Krojanker (Ger. P. 227492) prepares tar-oils for impregnating purposes with a high percentage of bitumen and resisting the effect of cold weather, by mixing 1 part of tar with 0·9 part crude benzol and removing the free carbon by a filter-press. The filtrate is freed from the solvent by distillation with steam, and the residue mixed with tar-oil. The washed carbon is purified and can be employed for the manufacture of electric carbons. The oil, prepared in this way, does not secrete any solid substances when exposed to cold; it is therefore easily transported, stored, and handled.

The advantages of pickling wood with tar-oils, or "creosoting," are both chemical and mechanical. The principal chemical action of coal-tar creosote was formerly ascribed to its "acids" —*i.e.*, the phenols—which certainly coagulate albumen, and consequently render animal life impossible. This, together with the now universal supposition that putrefactive decay can only occur in the presence of microscopic organisms, whose vital process is an indispensable condition of it, would by itself explain why timber impregnated with phenol cannot decay, provided that the phenol is not removed again by washing, etc. Hence the value of creosoting-oils would correspond to their percentage of phenols. But this opinion is generally contradicted now, and it is held that the "indifferent oils" participate essentially in the preservative action of coal-tar creosote. In any case the last-mentioned oils play a principal part in the *mechanical* effects of creosote oil, which are no doubt very important. The oil, being forcibly drawn into the wood by a vacuum and then driven in by high pressure, closes up all pores and, as it were, agglutinates all the parts so that no water can penetrate, without which living organisms cannot develop and the wood cannot decay. Even larger insects and other vermin are kept away by the smell of creosoted wood. This smell, however, has its drawbacks. It is sometimes so strong in pits fitted with creosoted timber that the men suffer a good deal from it, and the demand has even been raised to forbid the use of creosoted timber for coal-pits, etc., for this reason. Nor must it be overlooked that the danger of fire in the pits is decidedly increased thereby. It is therefore advisable to paint the creosoted timber with a silicate-of-soda paint, or something like it, which both stops the smell and prevents any danger of fire.

There are many undoubted instances of creosoted timber used for piers in salt water having successfully resisted even the formidable *Teredo navalis* during a long series of years; but there are also failures, sometimes in the same waters where the successful cases have occurred. The failure is caused either by the outer or creosoted part of the wood having been broken or cut off by the workmen in the process of construction, so that the worm could get into the inside of the timber; or by creosoting the wood in the wet state or imperfectly; or by employing creosote which is too thin, light, or volatile. Wood intended to resist marine insects should receive a heavier dose of creosote, and is better employed in the round state than squared, because the sap-wood more readily absorbs the creosote than the heart-wood, and thus forms a protecting girdle against the worm. (Private communication from Mr S. B. Boulton.)

Creosoted stakes in vineyards are said to keep out the *Phylloxera* (*Polyt. Notizblatt*, 1886, p. 304); but this does not seem to be quite certain. In the Hessian Rhine province, where all stakes are creosoted, that parasite has not been found, although it occurs in other places not far distant. The assertion that such stakes impart a creosote taste to the wine is absurd, and is entirely refuted by the experience gained in Hessia.

The Arad-Csanad Railway Co. (Ger. P. 53691) asserts that the pickling of timber is improved by following up the ordinarily used salts of iron, zinc, and copper by a rosin-creosote soap (creolin, p. 658). Similar proposals had been previously made by Vohl (p. 682), Kretzschmar (*Chem. Zeit.*, 1889, p. 31), and Wolniewicz (*ibid.*, 1889, p. 1089).

The creosote treatment is also applied to sails, ship's ropes, fishing-nets, etc., and protects these better than the usual tarring. The objects are first "tanned" by treating them with a dilute solution of glue and then with a bath of tanner's bark. Thus glue is precipitated within the vegetable fibre, which is now enabled to fix the creosote oil in the subsequent treatment and retain it even in sea-water.

Seidenschnur (*Z. angew. Chem.*, 1901, p. 437) made numerous bacteriological investigations upon the efficiency of coal-tar oil, from which the acid constituents (the phenols) had been removed, for preserving wood, comparing its action with that of zinc chloride. His experiments, carried out with the employment of *Penicillium glaucum* and *Mucor mucedo*, showed that the destroying action of tar-oils on these organisms has no connection whatever with their contents of phenols. It is indifferent whether the oil contains much or little or nothing at all of these "tar-acids." The action of coal-tar, deprived of the "acids," on those fungi was three times as strong as that of zinc chloride, and the presence of 0·3 per cent. of it in the soil completely stopped the growth of the fungi. Later on (*Chem. Zeit.*, 1909, No. 77) Seidenschnur impregnated wood sleepers, with progressive quantities of acid-free tar-oil, and exposed the wood to the wood-destroying fungi, to dry-rot fungus (*Merulius lacrymans*) and to *Polyporus vaporarius.* The oil was emulsionated by rosin-soda soap, the emulsion containing the equivalent of 6 per cent. tar-oil. The experiments showed that the application of 0·8 kg. of tar-oil per sleeper sufficed for protecting the sleeper, so that the impregnation of the sleepers on the large scale, when they take up 7 kg. of oil, effects a ninefold security. From impregnated sleepers which had been in the railway track for sixteen years, and showed no trace of deterioration by rot, an oil was extracted which consisted almost entirely of high-boiling hydrocarbons, containing neither phenols, nor bases, nor oils of low boiling points.

In any case the neutral oils play an important part in the *physical action* of creosote oil, which is of the highest importance, by preventing *water* from getting at the wood, without which no putrefaction can set in. Large insects and other vermin are kept off by the smell of the creosoted wood, which resists even the attack of that terrible worm, *Teredo navalis*, during many years. This has been proved several decades ago in England, France, Belgium, Holland, and by the annual reports of the German Naval Office.

The impregnation with tar-oil, moreover, imparts to the wood an *increased mechanical strength*, amounting to 12 to 18 per cent., according to a Report of the German Office of Telegraphs.

Christiani (who holds a high place in that German Office reports on the use of various conserving agents applied to wooden telegraph poles. The average life of these is:—

Poles impregnated with cupric sulphate .	11·7 years
„ „ mercuric chloride .	13·7 „
„ „ tar-oil . .	20·6 „
Poles employed without impregnation .	7·7 „

The *cost* of one cubic metre of such poles per annum is:

Impregnated with cupric sulphate . .	4·19 marks
„ zinc chloride . .	4·05 „
„ tar-oil . . .	3·01 „
„ mercuric chloride . .	3·86 „
Employed without impregnation . .	5·30 „

Quite analogous results have been obtained by the French Eastern Railways. As to the details of these trials we must refer to Schneidt (*Glaser's Annalen*, 1910, lxvi., No. 785), and to the same author's *Die Beschaffung und Verwendung buchener Eisenbahnschwellen*, 1910, p. 24.

Clark (*J. Soc. Chem. Ind.*, 1890, p. 1005) reports at length on the experience gained in America by pickling wood with coal-tar dead oil on the one hand, and with wood-tar creosote on the other. The former contains less water and is more easily treated in the creosoting cylinder. The wood-tar creosote is free from ammonia, less volatile, and less soluble in water, so that the advantages and drawbacks nearly counterbalance.

Another report on the application of the various wood-preserving processes has been made by Charnute in *Eng. and Min. J.*, 1900, p. 606.

Ziffer (*Stahl u. Eisen*, 1911, p. 364) gives the following comparison of the duration of railroad sleepers, made of various descriptions of wood, and treated by various methods:—

Description of wood.	Duration (years).				
	Not impregnated.	Impregnated with			
		Cupric sulphate.	Zinc chloride.	Zinc chloride + 10 per cent. tar-oil.	Tar-oil.
Oak . . .	12-15	14-16	16	18-20	25
Beech. . .	2-3	15-18	5-8	14-16	30-35
Larch. . .	6-8	12-15	9-15	15-18	18-24
Pine or fir . .	5-7	6-12	7-12	13-15	15-18

A detailed report on the conservation of wood for railway sleepers, telegraph and telephone poles, water-works, coal-pits, etc., has been made by Shipley (*Industrial Progress*, 1909, i., p. 539). According to him at that time the railroads in the United States used up more than a hundred millions of sleepers, only 16 to 20 per cent. of which were protected against destruction by being impregnated with various agents (apart from the wood used for telegraphic and telephonic poles, in coal-pits and other mines, and in hydraulic plants). Non-impregnated sleepers last in the Southern States only three years, in the Northern States from five to six years; sleepers impregnated by modern methods from twelve to fifteen years. Wood employed for marine constructions in the Southern States lasts only about three years, in the Northern States from five to six years; impregnated wood, from twelve to fifteen years. Such wood is at the southern coast destroyed by the *Toredo* after a twelvemonth if not impregnated, whilst timber impregnated with 20 lb. creosote oil per cubic foot lasts for twenty years. According to "Iron Age," 24th March 1910, 212,000 tons of tar-oils were consumed *per annum* in the United States for pickling railroad sleepers, only 30 per cent. of which was produced in the States. In 1909 the consumption of creosote oil in the United States was 51,431,212 gall.; 73 per cent. was imported from abroad.

At the Annual Meeting of the American Wood Preservers' Association at Chicago, in January 1915 (as reported in *Z. angew. Chem.*, 1915, iii., pp. 209 *et seq.*), several communications were made concerning the behaviour of creosoted railroad sleepers, etc. J. H. Waterman stated that undoubtedly the creosoting process was superior to all others for conserving sleepers or other descriptions of timber. Such sleepers hold out for twenty-five years, unless they have to be removed before this on account of mechanical wear and tear. L. F. Shakell described his experiments on the poisonous action asserted by coal-tar creosote on wood-destroying molluscs, which are less pronounced with the higher-boiling fractions. Similar observations were communicated by E. S. Christian and others. General rules were laid down by the Permanent Committee on Specifications for the Purchase and Impregnation of Timber.

Part played by Naphthalene in Pickling Timber.—It has long been disputed what part is taken by the naphthalene in creosote oil. We know that it occurs abundantly therein, and crystallizes out on the cooling of the first fraction of this oil. Its quantity is increased by the residue from working the light oils for benzols, phenols, etc., which is extremely rich in naphthalene, going to the creosote oil. This, as it arrives at the creosoting-works, is often quite pasty in consequence of the presence of a great deal of naphthalene. In the pickling process the oil is heated to 50°, so that the naphthalene is dissolved; and only on the cooling of the pickled wood does it crystallize again, among the other constituents of the oil, the coagulated albumen, etc. It was formerly believed that this was injurious to the preservation of wood, perhaps on account of the naphthalene volatilizing and leaving empty spaces which might be filled with moisture and become breeding-places for putrefactive organisms. Hence several creosoting-works have fixed a maximum for the percentage of naphthalene in the creosote oil sold to them, which causes great inconvenience to the tar-distiller, since very much more naphthalene is produced than can as yet be consumed.

But it seems that the objection to naphthalene in creosoting is quite unfounded. In the first place, naphthalene itself is undoubtedly a disinfectant and prevents the development of lower organisms. Secondly, as has been proved by Dr C. Meymott Tidy,[1] the total loss by evaporation of naphthalene is very small, and takes place almost exclusively during the first day or two after the wood has come out of the creosoting apparatus. During the first and second day some naphthalene volatilizes from the surface of the timber; but after this there is no more loss of weight, and the interior of the wood is quite unchanged. According to Dr Tidy, the naphthalene is useful both chemically and physically; it cannot possibly do any harm; and the condition that creosote oil should be free from it seems quite uncalled for. This is also generally recognized in America, where, according to Tayne (*J. Amer. Chem. Soc.*, xxii. (1900), p. 614), the specifications directly require 40 to 50 per cent. naphthalene to be present.

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[1] In an official (unpublished) report kindly placed at my disposal by Dr Tidy; compare later on his report of 1883.

Prescriptions concerning the Quality of Tar-oils, to be used for Pickling Timber.

These prescriptions have been very different in former times from what is considered suitable nowadays; and even now there are great differences in the rules laid down in various countries, and by railway and telegraph companies, more particularly concerning the amount of tar-acids (phenols), as we shall see *infra.*

The different *requirements concerning the quality of the oil* made by some English and foreign creosoting-works are stated in the table on p. 696.

Another table (from Allen's *Comm. Organ. Anal.*, 2nd edition, vol. ii., p. 555), given below, shows the general character of different descriptions of creosote oils. The samples under A were the whole runnings of heavy oils distilled from samples of tar obtained from twenty different Metropolitan gas-works. The samples under B were produced at the Beckton tar-works, and represent oils from which portions of the green oils and naphthalene were excluded; they are hence rich in tar-acids and rather less volatile than A. The liquefying-point of the B samples ranged from 36°·7 to 32°·8 C., and the point of turbidity on cooling from 31°·1 to 28°·3. The samples in series C are country creosotes, analysed by L. Archbutt. All were completely fluid at 32°, and many at 15°·6. The sample yielding 72 per cent. of distillate and 13·5 per cent. of tar-acids was the product of special treatment. The samples in series C are probably somewhat richer in tar-acids than the generality of country oils:—

	Spec. grav. at 32° C.	Percentage of distillate below 315° C.	Percentage of tar-acids from distillate.
A. Heavy London oils: highest	1·075	79	8·0
" " " lowest	1·048	60	3·0
Average of 20 samples	1·0588	71·5	5·6
B. Partial runnings from London oils: highest	...	91	10·2
Do. lowest	...	78	8·2
Average of 20 samples	...	82·8	9·15
C. English country oils: highest	1·056	90	24·0
" " " lowest	1·024	72	13·5
Average of 18 samples	1·0335	81·8	18·6

Specification made by . .	Dr Letheby.	Great Western Railway Co.	Chemin de fer de l'Est (France).	Chemin de fer de l'Ouest (France).	Chemin de fer de l'Etat Belge.	German Pickling Works "O."	German Pickling Works "M."
Spec. grav. .	1·045 to 1·055 at 60° F., but as nearly as possible at 1·050.	1·045 to 1·055 at 60° F.	1·030 at 35° C.	...	...	Between 1·020 and 1·055 at 15° C.	Between 1·055 and 1·100 at 15° C.
Deposit when cold.	Should not deposit any naphthalene at 40° F.	Should not deposit more than 30 per cent. at 40° F.	...	...	Not above 30 per cent. deposit (temperature not stated).	Entirely liquid at 15° C., as free as possible from naphthalene.	Free from naphthalene bottoms at 15° C.
Yield of coal-tar acids.	5 per cent. crude carbolic acid and other coal-tar acids.	10 per cent. acids, of which 5 per cent. crude carbolic acid.	8 per cent. phenol.	5 per cent. phenol.	...	20 to 25 per cent. tar acids soluble in caustic-soda solution, spec. grav. 1·15.	At least 10 p.c. by volume of carbolic acid, estimated by treatment of the oils boiling up to 400° C. with caustic-soda solution, spec. grav. 1·15.
Heat and quantity of distillate.	Should not yield less than 90 per cent. at 600° F.	Not less than 90 per cent. at 600° F.[1]	...	...	One-third should distil at 200° to 250°, two-thirds above 250° C.	To boil between 150° and 400° C. No more than 25 p.c. to distil below 235°, at most 1 p.c. below 125°. No fraction taken at intervals of 50° C. each, to separate more than 5 p.c. $C_{10}H_8$.	Nothing to distil below 150° C.; at most 25 per cent. up to 235°; to distil completely up to 400° C.
Heat and liquidity.	...	...	Should be perfectly liquid at 35° C.				
Further requirements.	...	...	...	Should be of "first quality."	...	Should be obtained entirely from coal-tar and possess a greenish-black colour.	

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[1] This requirement has been dropped since 1882.

The creosote oils distilled in London and from tar made of Newcastle coal are generally richest in naphthalene and high-boiling constituents, and contain but a moderate percentage of tar-acids. "Country oils," or oils from the Midland district, are lighter, thinner, and more volatile than "London oils"; they usually contain less naphthalene and more tar-acids. Scotch oils, which are largely derived from cannel coal, are still thinner and more volatile, and sometimes lighter than water.

The present state of the important question as to what is the best quality of coal-tar oil for creosoting purposes is very clearly elucidated in a report for which I am indebted to the kindness of Mr S. B. Boulton, and which is printed *in extenso* in the former editions of this treatise. In this edition we will only quote its salient points.

Liebig's theory of the destruction of organic substances by "eramacausis" is now antiquated, and so is the idea that putrefaction can be avoided by coagulating the albumen. The germ theory is now universally adopted, and we may take it for certain that antiseptics must either kill the germs, or prevent them from entering the substance, or both. The choice of antiseptics must be regulated by circumstances. For hygienic and therapeutic purposes the volatility and solubility of the antiseptics are frequently even of advantage, but for timber exposed to the atmosphere and to moisture it is otherwise. Here those antiseptics are more permanently successful which resist moisture and fill up the pores of the wood with substances inimical to the development of destructive organisms. Here, again, volatile oils, as petroleum, etc., have necessarily failed, and the creosote oils have proved to be the most successful. From 1838 to 1860 they were applied without much chemical research having been made about them. When the value of carbolic acid began to be recognised, it was considered the most potent agent in this case as well, but later on it was found that it is not so, carbolic acid (C_6H_5OH) being too volatile and soluble in water. The higher phenols contained in the heavier and later distillates are far superior for our purpose to carbolic and cresylic acid. Naphthalene is now also known to be a most useful antiseptic, and since all properly conducted creosoting operations are now carried on at a temperature of at least 50° C., it can be injected without the slightest difficulty.

Its after-consolidation within the pores of the wood is very useful, as it tends to resist the exudation of the more fluid oils, and the incursion of water and micro-organisms. Practical experiments, extending over a number of years, have shown that the carbolic acid, contained in creosote, disappears within twelve months, whereas wood treated with the heavier oils used for railway-sleepers, fences, etc., has been found perfectly sound by different investigators even thirty-two years after its being put into place. This timber contains no carbolic acid, but the heavier and less volatile oils, most of them not distilling under 300° C.; also acridine and cryptidines, and mostly naphthalene, sometimes in considerable quantities.

These opinions of Mr Boulton to a great extent coincide with those expressed in a report by Dr C. Meymott Tidy, made to the directors of the Gas-Light and Coke Company in 1883, and printed in our former editions. He does, however, attribute more importance than Mr Boulton to the coagulation of the sap albumen, brought about by the tar-acids. Otherwise these acids have but little value for preserving sleepers, etc., as they seem to be entirely dissipated within a very short time. The naphthalene does very great service, and so do the heavy oils distilling not under 600° F. (316° C.). This investigation led Dr Tidy to draw up a specification which follows here in the form given to it in 1885.

"*Dr Tidy's Specification for Creosote* (*as amended in* 1885).

"1. That the creosote shall be completely liquid at a temperature of 100° F. [38° C.], no deposit afterwards taking place until the oil registers a temperature of 95° F. [35° C.].

"2. That the creosote shall contain at least 25 per cent. of constituents that do not distil over at a temperature of 600° F. [316° C.].

"3. That, tested by the process hereafter to be described, the creosote shall yield a total of 8 per cent. of tar-acids.

"4. That it shall contain no admixture of bone oil, shale oil, or of any substance not obtained from the distillation of coal-tar; and that the first 25 per cent. of the distillate shall have a specific gravity greater than that of water.

"*Process to be adopted for determining the Coal-tar Acids.*

"1. One hundred c.c. of the well-mixed creosote is to be distilled at a temperature of 600° F. until no further distillate comes over. The distillate so obtained is to be mixed and well shaken in a stoppered flask with 30 c.c. of a solution of caustic soda, of sp. gr. 1200. The mixture is then to be heated. This done, the stopper is to be replaced in the flask, and the hot mixture again shaken vigorously for at least a minute.

"The contents of the flask are now to be poured into a separating-funnel (Fig. 156), and the soda solution drawn off. The creosote is to be heated a second and a third time in a similar manner with the caustic-soda solution, except that only 20 c.c. of the soda solution shall be used for the second and third extractions, instead of 30 c.c., as in the first extraction.

"2. The three soda solutions are now to be mixed together. *When cold*, any particles of creosote are to be got rid of by means of a separating-funnel. This done, the solution is to be thoroughly boiled, in order to expel the last traces of creosote present in the solution. The mixture is then to be allowed to cool. When cold, dilute sulphuric acid (1 of acid to 3 of water) is to be added (about 35 c.c. will be required) until the solution becomes slightly acid to litmus. The whole is then to be poured into a separating-funnel, and allowed to stand until perfectly cold, and the tar-acids well separated.

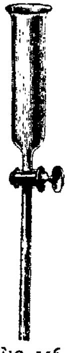
FIG. 156.

"3. The tar-acids are now to be dissolved in 20 c.c. of the caustic-soda solution (sp. gr. 1200) and 10 c.c. of water. The mixture is then to be boiled and filtered through a funnel fitted with a plug of asbestos. The asbestos plug is to be washed with not more than 5 c.c. of boiling water. The solution is to be allowed to cool *perfectly* in a 100 c.c. measure. It is then to be rendered slightly acid with dilute sulphuric acid (1 to 3) (10 c.c. will probably be found sufficient for this purpose). The whole is again allowed to stand *for two hours* until *perfectly cold*, when the percentage of the tar-acids is to be read off.

"*Process to be adopted in estimating the Quantity of Distillate.*

"The operation is to be conducted in a retort (fitted with a thermometer), and heated with the naked flame of a Bunsen burner. The heat applied is to be gradually raised to 600° F., and continued at that temperature until no further matters distil over. The distillation of the 100 c.c. should be completed within half an hour."

The above has been entirely upheld by a new report, made by Dr Tidy to the Gas-light and Coke Company on 11th February 1885, in reply to a paper by Dr Voelcker and to the specification suggested by that gentleman. We now append the reasons given by Dr Tidy for some of the above details:—

"1. The omission of any clause specifying the specific gravity of the creosote to be used. I have done this advisedly, because of the extreme difficulty in taking the gravity of creosote at normal temperatures with the 1000-grain bottle, and the practical uselessness in my judgment of employing a hydrometer for the purpose. If it be considered necessary to introduce a specific-gravity clause, I would suggest that the gravity be between 1040 and 1065, water being 1000. I am of opinion, however, that for practical purposes a specific-gravity clause is altogether unnecessary.

"2. Believing strongly as I do in the value of those constituents of the oil that are the most difficult to volatilize, I have deemed it right to suggest a clause to the effect that the creosote shall contain at least 25 per cent. of matters that distil over above 600° F.

"3. I have made a large number of experiments as to the best method by which the estimation of the tar-acids may be determined.

"I note—

"(*a*) That very slight differences in the strength of the solutions used, and in methods of manipulation, considerably influence the results obtained. I therefore deem it necessary that, as a part of the specification, the process to be employed for estimating the acids should be exactly stated.

"(*b*) I have failed to discover any easy method of separating the carbolic from the other tar-acids. I have tried for this purpose numerous experiments, but with such unsatisfactory results that I have decided to recommend that the total quantity of tar-acids only should be stated. Further, the fact that as preservatives one kind of tar-acid is, so far as we know, as good as any other, renders a further separation of the acids in my judgment unnecessary. My analyses of samples will show that in fixing not less than 8 per cent. of total tar-acids, we obtain a fair index of the purity and genuineness of the creosote."

We now give

Sir F. Abel's Specification, 2nd January 1884, *for Creosote.*

"The creosoting liquor is to be of the description known as heavy oil of tar obtained by the distillation of coal-tar, and consisting of that portion of the distillate which comes over between the temperature of about 350° F. (176° C.) and that of 760° F. (405° C.).

"The liquor must be free from admixture with any oil or other substance not obtainable from such distillate. It shall contain not less than 20 nor more than 30 per cent. of constituents that do not distil over at a temperature approaching 600° F. (316° C.).

"It must yield not less than 9 per cent. by volume of tar-acids when tested in accordance with the instructions annexed.

"The creosoting liquor must become completely fluid when raised to a temperature of 100° F. (38° C.), and exhibit no signs of any deposit on cooling down to a temperature of 90° F. (32½° C.).

"The specific gravity of the liquor must not be less than 1·035, and not more than 1·065 at a temperature of 90° F., as compared with water at 60° F.

"*Test for Creosoting Liquor.*

"1st. The liquor, if necessary, is to be warmed until it is perfectly fluid.

"A. One hundred c.c. is then to be placed in a glass retort of convenient size, and subjected to distillation until a temperature of nearly 600° F. is attained.

"The thermometer regulating the temperature must be so placed in the retort that at the commencement of the distillation the bulb of the thermometer is entirely immersed in the liquid, but not touching the bottom of the retort. The distillate should be collected in a stoppered-glass bottle, having a capacity of about 200 c.c.

"2nd. The distillate is to be mixed with 20 c.c. of a solution of caustic soda (sp. gr. 1·21), the mixture being shaken at intervals for a period of not less than three hours, and is then to be transferred to a burette provided with a glass tap, into which has previously been introduced a few drops of soda solution sufficient to fill the narrow space above the stopcock. The burette, with its contents, is then to be set aside for twelve hours, in a place sufficiently warm to keep the liquid fluid. The soda solution containing the tar-acids will then be found to have separated from the other portions of the creosoting liquor, occupying the lower portion of the burette, and should then be drawn off into a small glass flask, which should have a capacity of about 100 c.c., and be provided with a long narrow neck (divided into cubic centimetres) of sufficient length to be capable of holding the whole of the tar-acids afterwards separated. The liquor not acted upon by the soda solution is to be returned to the bottle by inverting the burette. Ten c.c. of fresh soda solution is then to be added, and the mixture again treated as before. The soda solution from this second treatment, containing any further amount of tar-acids not extracted by the first treatment, is then to be added to the soda solution first obtained in the long-neck flask. Sulphuric acid, dilute (1 vol. of oil of vitriol and 3 vols. of water), is now to be gradually introduced into the flask until a very slightly acid reaction is produced, the flask being kept cool. Then enough mercury is poured into the flask to drive all the tar-acids up into its neck, where their volume can be read off on the graduation.

"*Note.*—If the creosoting liquor is of an unusually thick consistency, it may be found necessary to subject it to a preliminary distillation, which should be conducted as described at A; but the use of a thermometer is not necessary, as the distillation should be continued until nothing further comes over."

Abel's specification very nearly agrees with Tidy's, and the separation of carbolic and cresylic acid by fractional distillation of the tar-acids, formerly prescribed by Sir F. Abel, but objected to by me in the first edition of this treatise (p. 208) as quite illusory, has been dropped. Tidy's prescription of boiling the alkaline solution of the tar-acids, in order to expel any hydrocarbons, is, I think, quite called for; but then Abel requires 9 per cent. in lieu of 8 per cent., which will compensate for the impurities left by his treatment in the tar-acids.

The *tests made at the works* are mostly more simple than the above. The *density* is best ascertained at about 32°, when the oils are all fluid, by means of a hydrometer, or else by a specific-gravity bottle, which is allowed to cool down to 15°, when the stopper is pressed in tightly. The *liquefying-point* is found by placing some of the oil in a test-tube, inserting a thermometer and moving about in a warm-water bath; the *point of turbidity*, by allowing the whole to cool down. The *distillate up to* 315° is found by heating 100 c.c. in a 4-oz. retort by a small naked flame, protected by a tin cylinder. The thermometer ought just to touch the liquid remaining at the end. The distillation should last about thirty minutes. The *tar-acids* are usually estimated in the distillate by treating it twice with 30 and 15 c.c. of caustic-soda solution of sp. gr. 1·21, at a gentle heat, separating the oil by a tap-funnel, cooling down, adding 30 c.c. of dilute sulphuric acid (1 acid to 3 water, transferring to a graduated cylinder), allowing to *cool completely*, and reading off the volume of tar-acids separated (Messrs Burt, Boulton, & Haywood).

If the *basic constituents* are to be estimated, the rules mentioned in Chapter X. must be observed.

A specification of the Prussian Railroad Management for impregnating oils, issued in 1904, contains the following conditions:—"The tar-oils must be composed in such manner that on distilling them (the thermometer being kept in the vapour) up to 150° C., at most 3 per cent., from 150° to 255° at most 30 per cent., and from 150° to 355° at least 85 per cent., pass over. The specific gravity at 15° is to be between 1·04 and 1·10. At this temperature the oil should be perfectly clear, and show no secretion of solid naphthalene when a few drops are poured upon a layer of filtering paper. Its percentage of phenolic substances, *i.e.*, such as are dissolved by caustic-soda solution of sp. gr. 1·15 at 15°, should be at least 10 per cent."

Kraemer and Spilker state that these conditions are fulfilled by a mixture of equal parts of creosote oil and filtered anthracene oil, but that they cannot be fulfilled by oils containing more than 20 per cent. phenols, unless the former method (keeping the bulb of the thermometer within the liquid) be admitted.

The testing for phenols, according to that specification, is performed by shaking 100 c.c. oil with 100 c.c. caustic-soda liquor of sp. gr. 1·15 at 15° C. in a graduated 200 c.c. cylinder, allowing to stand for three or four hours, and observing the reduction of the volume of the oil, which is taken as indicating the percentage of phenols.

In the United States, according to Shipley (*Industrial Progress*, 1909, i., p. 539) the following prescriptions are made for tar-oil destined for impregnating purposes. It ought to be a pure coal-tar oil, free from other oils, perfectly liquid at 38°, and free from suspended solid substances. Its specific gravity at 38° ought to be at least 1·03. On being distilled from an 8-oz. retort, placed on asbestos, and fitted with a correct thermometer, the bulb of which is half an inch above the surface of the liquid, no more than 5 per cent. should pass over below 200°, and no more than 25 per cent. below 235°, and the residue remaining in the retort, after reaching 355° if it amounts to more than 5 per cent., should be soft. The oil should not contain more than 3 per cent. water. (Nothing is said here about the percentage of naphthalene. *Cf.* Tayne, *supra*, p. 694, nor about tar-acids, which is confirmed by Forrest, *supra*, p. 581.)

R. Lamb, in a lecture given at the American Society of Civil Engineers (*J. Gas Lighting*, 1911, cxiii., p. 521) quotes the following as the correct specification. The creosote oil ought to have a specific gravity not below 1·03, nor above 1·07 at 38° F. The fractional distillation of 100 c.c. ought to yield the following percentages of distillate (dry):—

Up to 150° (302° F.) . . .	nothing
Between 150° and 170° (338° F.) .	not above 5 per cent.
„ 170° „ 235° (455° F.) .	„ 35 „
„ 235° „ 300° (572° F.) .	„ 35 „

The residue ought to be soft. The oil should contain at least 25 per cent. naphthalene, and 15 per cent. anthracene oil. Ninety-five per cent. of the creosote oil should be soluble in carbon disulphide or absolute alcohol.

According to Church (*J. Ind. Eng. Chem.*, 1911, p. 231) the American Railway and Maintenance of Way Association has laid down the following prescriptions for the testing of creosote oil. The "Standard Creosoters' Distillation" is carried out in a tubulated retort, in which exactly 100 g. oil are placed. The bulb of the thermometer is half an inch above the level of the liquid; the distance between that bulb and the end of the condensing-tube should not be less than 20 or more than 24 in. The thermometer remains in the same place during the whole distillation, which is carried on without interruption, and which should last about forty-five minutes. The fractions are singly received in small flasks, and their quantity determined by weighing. These fractions are taken: (1) up to 170°; (2) from 170° to 200°; (3) from 200° to 210°; (4) from 210° to 235°; (5) from 235° to 270°; (6) from 270° to 315°; (7) from 315° to 355°. For practical purposes it is sufficient to make the following fractions: (1) below 200°; (2) 200° to 210°; (3) 210° to 235°; (4) 235° to 315°; (5) above 315°. If the oil contains water, the first distillate is separated into oil and water by means of a tap-funnel, and the oil put back into the retort. In this case first 500 to 600 c.c. are distilled in a copper still, and the dehydrated oil is distilled as above. The percentages are reduced to dehydrated oil, and the contents of water separately stated. The *tar-acids* and the *naphthalene* are estimated in one and the same operation, by distilling 100 c.c. of the liquefied oil in a flask of Jena glass, until 95 c.c have passed over, which should be the case within twenty minutes. The distillate is warmed up to 60° in a graduated separating-funnel and shaken up with 50 c.c. of 10 per cent. caustic-soda solution, and this operation is repeated another time, or even twice, until no more decrease of volume takes place, always at 60°. The total decrease of the volume of the oil is calculated as showing the *tar-acids*. For estimating the *naphthalene*, the oil contained in the separating-funnel is put into a copper beaker and kept during fifteen minutes at 15°·5, after which time the liquid is drawn off from the crystals by means of a porous funnel. The crystals are pressed till dry between layers of blotting-paper by means of a small hand-press, and their weight per cent. is calculated on the weight of the original volume of oil, as found by its specific gravity. The "stock point" of the oil is found by cooling 5 c.c. of the original oil, after heating it up to 60°, in the air, or in case of need in water, stirring it up with the thermometer until the first crystals appear.

Church also describes the *sulphonating-test*, as carried out in America. To the fraction of the tar-oil boiling between 305° and 320°, four or five times its volume of concentrated sulphuric acid is added, the mixture is heated up to 60°, and put ino a separating-funnel, graduated in its lower part. The remainder left in the flask is rinsed out three times by concentrated sulphuric acid. The mixture contained in the separating-funnel is carefully shaken for fifteen minutes, and allowed to stand overnight. Then the acid is carefully drawn into the graduated part of the funnel, so that 2 c.c. of it are left standing below the non-sulphonated oil. Whether such a remainder be noticed or not, the test is carried on as follows:—About 20 c.c. of water is added, and the mixture allowed to settle for half an hour, whereupon the aqueous liquid is carefully drawn off from the supernatant oil (or emulsion). Now 10 c.c. concentrated sulphuric acid is added to the contents of the funnel, and the mixture allowed to stand for fifteen or twenty minutes. Any non-sulphonated oil is now separated in a clear state, and its volume exactly read. The cubic centimetres found are calculated as per cent. by weight. If the non-sulphonated oil should have a strongly dark colour, it is treated with an excess of 10 per cent. caustic-soda solution. If thereby the oil is dissolved, the result is to be considered as negative.

Decomposition of Heavy Tar-oils by Heat (cracking).

This is sometimes done in order to utilize otherwise comparatively valueless oils or oily residues by exposing them to a high degree of heat—*e.g.*, passing them through red-hot tubes ("cracking"). Usually the main object was that of making illuminating-gas; but with this was associated the getting of more valuable oils. We have seen above (pp. 187 *et seq.*) that both benzol and anthracene can be obtained in this way from the heavy residues of petroleum, browncoal-tar, and wood-tar. Many chemists have worked in this direction, as Breitenlohner,[1] Vohl[2] (who believes this process to be practicable), Walker and Smith,[3] and others. [Kraemer (priv. comm.) declares the hydrocarbons of coal-tar to be much less suitable for the "cracking process" than the paraffins, especially petroleum distillates; the former yield but a small quantity of benzol, etc., or of illuminating bodies in general.] An apparatus specially constructed for the purpose in question was patented in 1861 by the Paris Gas Company;[4] it is represented in Fig. 157. It consists of a set of cast-iron cylindrical retorts, *a*, closed at one end and provided at the other end with a movable cover. About 12 in. from one end there is a partition, *b*, 8 or 12 in. high, which prevents the oil from running towards the part not exposed to the fire. The space thus shut off communicates by an ascending pipe, *c*, with a receiver, *d*, which is connected by *e* with another receiver, *d'*, both alike intended for heavy products of condensation: these are removed by the pipes *g g'*; whilst the vapours not yet condensed pass through the worm *f* and are collected in *h*. *l* carries away the incondensable gases. The heavy oil runs from the tank *k* through a tap, *j*, into the funnel *i*, and thence in a continuous stream into the retort *a*, previously brought to a red-heat. There the oil spreads as far as the partition *b*, and is decomposed into graphite (remaining in the retort) and volatile products (passing over the partition and through the pipes into the receivers). In *d* and *d'* a heavy, tarry liquid condenses; it is mixed with more heavy oil, and again run back into the retort [nowadays it would probably first be worked for anthracene]. The liquid condensed by the worm *f*, and collected in *h*, is rich in benzol, and is treated like ordinary crude naphtha. The gas escaping at *l* is employed for lighting, and was considered the principal product.

Behrens[5] employed for a similar purpose a retort made of firebricks, heated from below. It was heated up to a very bright red-heat; and a continuous jet of heavy oil was run into it by a swan-neck pipe. The volatile products were condensed by an ordinary hydraulic main and by very wide pipes, which nevertheless were frequently choked up with naphthalene and soot. In the hydraulic main (at the base of the furnace) most of the undecomposed oil was condensed; the remainder, together with naphthalene and the more volatile hydrocarbons newly formed, condensed in the cooling-pipes. In this way the

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[1] *Dingl. polyt. J.*, clxvii., p. 378; clxxv., p. 392. [2] *Ibid.*, clxxvii., p. 58.

[3] *Wagner's Jahresber.*, 1867, p. 752.

[4] *Technologiste*, 1861, p. 145; Girard & Delaire, *Dérivés de la Houille*, p. 20.

[5] *Dingl. polyt. J.*, ccviii., p. 361.

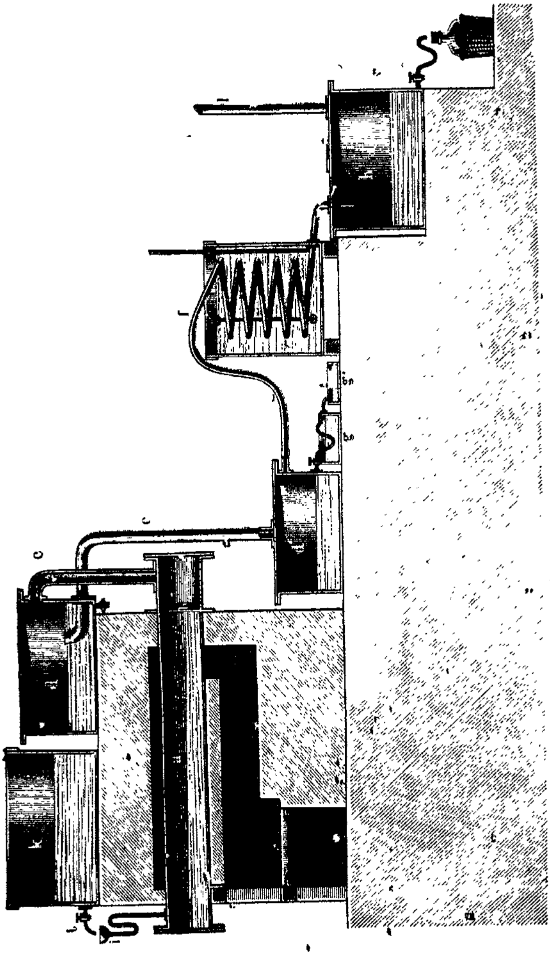

FIG. 157.

heavy oil yielded on an average 2 per cent. benzene and toluene, and a little xylene and higher homologues. Below and above the temperature just mentioned, less of the more volatile hydrocarbons was formed. In the former case but little heavy oil was decomposed;[1] in the latter the benzene was converted into naphthalene. In the furthest part of the condensing-apparatus, naphthalene, benzene, and toluene were collected. The graphite remaining on the furnace-bed could be obtained in large pieces, and was valuable for producing high temperatures.

Of course the apparatus employed at Nobel's works, at Baku, for decomposing petroleum residues (p. 190), might also be used for creosote oil.

G. E. Davis's proposal to convert all the distillates from tar, except naphthalene and anthracene, into gas, as described on pp. 68 *et seq.*, may be mentioned in this connection.

Kenyon (B. P. 13627, of 1887) passes steam and heated vapours of tar-oil, with a little air, into two retorts filled with coal, conducting the gases from the retorts charged later on into that charged at first. If it is intended to increase the yield of ammonia and aromatic hydrocarbons, the retorts are charged with coal rich in H, O, and N, together with waste leather, hair, etc. The escaping vapours are freed from anthracene and aromatic hydrocarbons by washing with heavy oils, cooled down to the freezing-point. (*Cf.* Kraemer's opinion on the Dinsmore process, p. 318.)

Formerly it would rarely have paid to convert tar-oils into gas; at present the price of creosote oil would be no obstacle to this process, but it is very doubtful whether there is any advantage in it (*cf.* L. T. Wright, p. 347).

According to J. Young, heavy paraffin oils can be converted into light ones by heating them in strong iron boilers under a pressure of 1½ atmospheres. Possibly this would apply also to heavy coal-tar oils; but evidently nothing can be said as to the probable cost, yield, and so forth.

Boleg (*cf.* p. 603) studied more closely the distillation of creosote oil under pressure. When employing 3 or 4 atmospheres' pressure and purifying with sulphuric acid and caustic-soda solution, a lighter, thinner, orange-coloured oil, almost devoid of smell was obtained, which might be used in the same way as "carbolineum" (p. 605), even for inside work. The naphthalene contained in the crude oil was also easily obtained, but no lighter oils.

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[1] Hence the cast-iron retorts patented by the Paris Gas Company (p. 707) cannot have stood a very long time, as they would have to be heated too high.

G. Schultz (Ger. Ps. 101863 and 105582) introduces creosote and anthracene oil into the gas-retorts and coke-ovens during the distilling process, thus converting those oils into more valuable hydrocarbons, such as benzol.

On p. 368 we have already mentioned Wirkner's process (B. P. 13185, of 1903; Ger. P. 158731), who converts tar "or tar-oils" into pitch by heating with sulphuric acid, and the process of the Chem. Fabr. Flörsheim Dr Nördlinger, which consists in heating tar or tar-oils to 120° to 150° C. in the presence of air, oxygen, or ozonized air, until the derived product has been obtained.

Planes, Ltd. (Birkenhead) and W. P. Thompson (B. P. 5245, of 1913) perform the cracking of heavy hydrocarbons by heating them in a still, together with finely divided nickel, acting as a catalyzer, and hydrogen or purified water-gas, with strong agitation, at a temperature of 300°, and a pressure of from 5 to 100 lb. per square foot. The gases escaping out of the condenser can be utilized as fuel. The nickel is regenerated from the NiO formed by washing this with benzol, igniting the oxide, transforming it into nitrate or formate, and reducing in a current of hydrogen at 320° to 350°.

Many patents have been taken out for decomposing heavy tar-oils by heat so as to render them, or the products obtained therefrom, available for driving motors of all kinds (*cf. supra*, p. 678).

Valpy and Lucas (B. P. 20470, of 1913, and 2838, of 1914) spray steam superheated to a temperature slightly below the cracking point into the oil in a still, and pass the mixture of oil, vapour, and steam through heated catalyzing tubes of nickel, which may be packed with catalyzing material, and thence to a coil in the oil still where the heat of the cracked vapour is utilized for heating the oil. The catalyzing tubes may be heated electrically, or by an oil burner.

Melamid and Grötzinger (Ger. P. 276775) obtain low-boiling hydrocarbons from tar or heavy tar-oils by heating with phosphoric acid in the presence of indifferent gases or vapours, such as nitrogen, steam, hydrogen, carbon dioxide, or air, at temperatures below 200°. When the oils obtained are treated again in the same manner, they are again cracked, yielding hydrocarbons of still lower specific gravity, very well adapted as a substitute for benzine in automobile cars. According to their Ger. P. 278192 this process may be carried out also in the absence of indifferent gases or vapours if care is exercised that the phosphoric acid is finely divided.

Another patent is that of the Gesellschaft für Verwertung von Kohlenstoffverbindungen, Ger. P. 284118.

Application of Creosote Oil for the "Blue-steaming" of Bricks.

The ancient Romans, as is shown by ash-urns, etc., understood the process of imparting to earthenware a fine slate-grey colour. They effected this by putting green wood into the brick-kilns, after finishing the burning process proper, and keeping the kilns closed; and this process is in use at the present day in Holland, where alder-wood is employed for the purpose. These Dutch "blue-steamed" bricks are extensively employed on account of their pleasing colour and their resistance to the weather.

In Germany the agent universally used for this purpose is creosote oil freed from naphthalene by keeping through the winter season. When the bricks have been sufficiently burnt, all openings in the kiln are closed with clay or sand and the damper let down. The oil is then run in through cast-iron pipes passing through the brickwork, in small portions at a time. The oil is at once vaporized and decomposed, carbon in the graphitic state being deposited on the surface and in the pores of the bricks and staining these grey with metallic lustre. When enough oil has been run in (as known by experience), water is run through the same pipes in several portions; this cools the bricks, so that the carbon is not burned on contact with air, and the quicker the cooling, the finer the colour.

This process must be carried out in periodically working, very strongly built kilns. Ch. and I. Lengholz (Ger. P. 95882) describe a special kiln for this purpose. Ludowici (*Tonindustrie Zeitung*, 1898, p. 38) shows that porous material is better than dense bricks, as is easily understood. The iron salts must also be reduced to protoxide, which greatly influences the colour. One thousand bricks require on the average 20 kg. of blue-steaming oil, but this depends on the percentage of iron. The opinion of Hoffmann (*ibid.*, 1898, p. 38), that in this process a kind of asphalt is formed, is not very conclusive, considering the high temperature.

The filling up of the pores with graphite would easily explain the greater resistance to the rain and frost, claimed for these bricks.

Various other Applications of Creosote Oil.

Nördlinger (Ger. P. 171380) makes pitch from it; he employs the same process for tar-oils as has been described in Chapter IV., viz., a treatment by air at 120° to 150° C.; *cf.* p. 369. Applied to the processes of Wendriner (Ger. P. 170932) and the Société anonyme des combustibles industriels (Ger. P. 161950; B. P. 16182, 1905).

Some other uses of creosote oil have been already mentioned in previous chapters, because they coincide with the uses of raw tar or anthracene oils. We mention of these:—The softening of *hard pitch*, p. 537; the preparation of *varnishes*, p. 549.

Bowden & Dodd (Ger. P. 126623) employ heavy tar-oils, distilling between 260° and 280° C., to mix (in the proportion of 11 per cent.) with rosin, fatty oils, and soapstone for the production of a water-tight and insulating compound.

Bilfinger (Amer. P. 729838) treats creosote oil with dry powdered alkali, air, and lead oxide, and then mixes it with cotton-seed oil, to produce a substitute for linseed oil.

The Manufacture of Lampblack and Soot from Tar-oils.

Formerly lampblack, which is the most important raw material for printers' ink and for many black paints, had to be made by burning rosin or rosinous wood. The introduction of coal-tar has completely revolutionized this manufacture, which is described in a special treatise by H. Köhler (*Die Fabrikation des Russes und der Schwärze*, 3rd ed., 1913).

Raw tar is not very well adapted for it, owing to the presence of water and volatile substances, which make the soot impure and sometimes yield explosive mixtures. Therefore, just as in the manufacture of roofing-felt, the tar is deprived of those substances by partial distillation; or else "prepared tar," creosote oil, or pitch are employed. The coarsest quality of soot is obtained from pitch; then follow "prepared tar," partly distilled tar, and best of all creosote oil. Lampblack proper is always made from gaseous or vaporized raw material (benzol, etc.).

The tar or tar-oil is burned from soot in brick furnaces, connected with long brick flues, where the smoke-gases can deposit the flakes of soot before escaping into the air. Engler (*Chem. Ind.*, 1885, p. 395) describes this industry as carried on in the Black Forest, where about 250 tons per annum are made in the following way:—

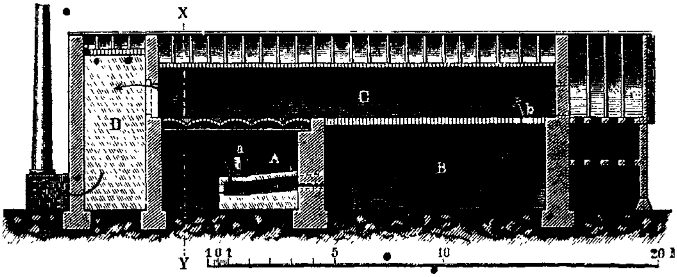

FIG. 158.

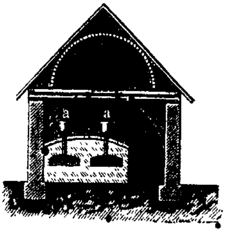

FIG. 159.

Figs. 158 and 159 show the furnaces A, into which solid pitch, etc., is charged by hand; tar or oils are run in by pipes from the vessels *a*. The smoke travels first into the cooling-vault B, then through *b* into the long vault C, then into the tower D, divided into two compartments by a perpendicular partition, and through a damper into the chimney. The last portions of soot are retained by a coarse fabric extended across one-half of the tower. The work is commenced on Tuesday, is daily interrupted from 9 P.M. till 5 A.M., and continued till Saturday. During Sunday the furnace cools down, so that the soot can be taken out on Monday.

These furnaces do not provide for cooling the flame, which is, however, preferable for obtaining a better yield of soot. An improved furnace (according to Köhler) is shown in Figs. 160 and 161. *a* is a cast-iron fire-plate, angularly shaped, so that the liquid fuel cannot run out in front; *b* is a conical cooler of ¼-in. sheet-iron, with a tight-fitting cover, manhole *f*, steam-pipe *g*, gauge-cock *e*, and running-off tap *q*. The liquid fuel is supplied through the 2½-in. pipe *d*, from the heater *n* to the fireplace *p*, and runs out of small bent pipes regulated by a tap. These small pipes can be turned sideways in their sockets, when solid material (pitch) is to be charged by hand. The fireplaces *p* are provided with a slide-door, adjustable in any position by toothed gear; *c* is a square flue made of sheet-iron 12 ft. long, for conveying the gases through the cooler *i* into the chambers *k*; *h* is a channel, kept full of water by means of a tap, to extinguish the coke falling out of the fire and removable by the door *m*.

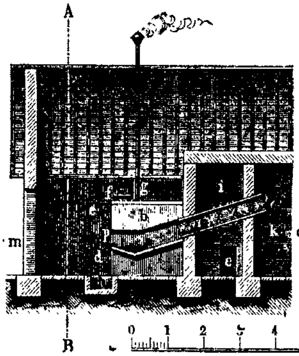

FIG. 160.

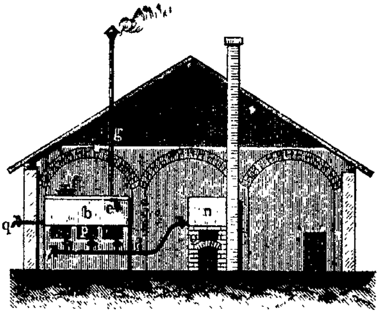

FIG. 161.

The chambers *k* consist of three parallel vaults, each about 120 ft. long, through which the smoke-gases travel in succession before escaping through the 50-ft. chimney. These vaults are provided with a number of inside partitions, causing the gases to travel consecutively along the bottom or top of the chamber. All the compartments thus formed are connected by iron doors one with another, and at the end opposite the fire with a common collecting and packing room.

To begin with, a good fire is made on the fire-plate *a* by means of paper, tarred or oily cotton-waste, etc., and then the material to be converted into soot is charged. Every day about 15 cwt. of tar or pitch, or from 20 to 24 cwt. of tar-oil can be burned, the work being carried on as described in the Black Forest. All doors leading outside must be kept tight by pasting paper over the joints, as a precise regulation of the draught is very important to obtain a good yield, which should be 25 per cent. from tar and 18 to 20 per cent. from pitch, and 25 to 30 per cent. from creosote oil.

This arrangement permits of utilizing the heat of the fire for evaporating large quantities of liquid, as is easily understood.

The following description of lampblack-making has been given by Nepp (*Chem. Zeit.*, 1878, p. 222). The tar is employed for heating six steam-boilers 13 ft. long, 2 ft. 2 in. in diameter, which jointly supply an 8 h.p. steam-engine. The tar is run into tanks holding two barrels each, one in front of each boiler. Behind the boiler is an oven, in which the gases from the burning tar, which have been partially cooled in their course through the boiler-flues, deposit the soot contained in them upon horizontal and vertical shelves, which divide the oven into several compartments. The lightest particles of soot are deposited in the highest part of the oven; and this does not require to be so often emptied as the middle and lower shelves, which contain most of the lampblack, and are emptied directly after the tar has been burnt off. The work lasts six hours and proceeds by turns, three ovens continually going together, so that there is always enough steam. In the fireplace a residue of fine coke is found. The ovens are well bound and covered with metal plates. They are 13 ft. high; the upper 3 ft. project through the roof, so that they are cooled from without. They are accessible from below by an iron door, from above by iron steps. The lampblack is partly left as it is; but most of it is mixed with peat, finely ground under edge-rollers, and sifted before it is sent out. The steam generated in the boilers is employed for driving a peat-mill, manufacturing the casks, etc. The cost of plant is about £400 to £450. The product serves for manufacturing colours, shoe-blacking, black-lead for stoves, etc.

According to Newton's patent of 1854, lampblack can be obtained directly by mixing 160 lb. of coal-tar with 200 lb. of slaked lime, adding 18 lb. of alum, and strongly heating the well-kneaded mixture without access of air in fireclay crucibles or iron cylinders, as in preparing bone-charcoal. The product should be allowed to cool down without access of air, and is at last finely ground. By altering the proportions of tar and lime, all shades between brown and grey can be obtained.

Wegelin (Ger. Ps. 129647 and 138940; B. P. 13837, 1903) heats the tar to boiling and burns the vapour, by injecting the previously heated air into the boiling tar, thus obtaining pitch as a by-product. An additional patent (Ger. P. 179179) protects the utilization of the radiant heat of the mixture of gas and air, and the agitation of the boiling tar by injecting carbonic acid or steam, or by mechanical stirring, for the purpose of preventing the superficial formation of slag and coke.

The Kölner Russfabriken (Ger. P. 133270) burn the tar incompletely without previous distillation, obtaining pitch as a by-product.

Irvine (*Chem. Zeit.*, 1902, Rep., p. 80) causes the soot to precipitate more quickly by means of the electric current.

Hartmann (Ger. P., Anm. H26230) aims at increasing the density of the soot.

Ogilvie obtained a German patent (No. 148258), which lapsed already in 1904, for directing the flame of tar immediately on the surface of water.

A long paper on the manufacture of soot has been published by Luhmann in *Asph. u. Teer-Ind. Zeit.*, 1903, pp. 511, 530, 545.

Maechtolf (*Z. angew. Chem.*, 1908, p. 1088) has taken two German patents for the manufacture of lampblack. According to the first, No. 194301, of 1905, he employs a decomposing cylinder, in which he produces lampblack from hydrocarbons by means of the electric arc, or by fulminating mercury. This cylinder is provided with an agitator and is connected with a soot-collector, in which a press-piston moves up and down, and to which is attached an arrangement for packing the barrels.

According to his second patent, No. 194939, of 1905, lampblack of specially good quality is obtained by pre-heating the hydrocarbons to be decomposed, and at the same time subjecting them to variable pressure; also by mixing them with hydrocarbons decomposed at lower temperatures (such as acetylene), first in larger, then in smaller quantities, until the temperature has risen to such a height that the heavy hydrocarbons are decomposed without admixture.

The Rütgerswerke A.-G. (Ger. P. 208600) improve the yield of lampblack, which hitherto amounted to 20 to 25 per cent. from tar, or 12 to 15 per cent. from pitch, 50 to 60 per cent. remaining as coke in the fireplace. It is better to extract the tar or pitch by suitable solvents—*e.g.*, naphthalene—to separate the remaining carbon from the solution, and to work the latter either as a whole, or after volatilizing the solvent, for lampblack by inflammation in the usual manner.

Thenius (*Die technische Verwendung des Steinkohlenteers*, p. 132) describes several lampblack furnaces of a very simple kind, intended for burning tar-oils, pitch, etc. The furnace for "soot-oil" consists of a metal plate kept red-hot from below by a local small fire; it forms the bottom of a brick chamber. Upon this the "soot-oil" constantly drops in a fine stream from a tank, whilst a side door with small holes admits the air necessary for combustion. The smoke enters four brick chambers, communicating with a chimney. When the oil intended for combustion has been used up, the furnace is left standing for a few days, and the four chambers are opened by doors provided for the purpose. The last chamber (next to the chimney) contains the finest lampblack (for lithographers); the third one the next finest (for printers); the second and first contain coarser soot, which is well sifted and sold as common lampblack. The best kind is sometimes further refined (for paper-makers, colour-manufacturers, lithographers) by ignition in sheet-iron cases, the covers of which are luted with clay. They must be heated for some time in a furnace with a good draught, till all empyreumatic oils have been driven off, and the soot remains behind without any smell. The cases must be left to cool for several days before opening them, because the soot cools very slowly and would take fire if it were exposed to the air too soon. This is "half-calcined lampblack"; the "thoroughly calcined" article is obtained by igniting the first product once more in fresh cases and treating it as above. Four hundred pounds of "soot-oil" (*i.e.*, heavy coal-tar oil) should yield 20 lb. finest lampblack, 30 lb. seconds, and 23 lb. of the third and fourth qualities. On the metal plates some coke remains, which is knocked off and sold as fuel.

The English plan of calcining soot consists in putting a small portion into a circular iron pan, about 2¼ ft. high and 2¼ ft. in diameter, lighting it by a red-hot iron, and adding more from time to time as the ignition proceeds. When the pan, being full, ceases smoking, the cover is put on and its contents are allowed to cool. There is about 25 per cent. loss in this process, which should be conducted in a well-ventilated, closed building.

J. Brönner (private communication) burns all waste products of tar-distilling under a specially constructed steam-boiler of somewhat complicated construction, and forces the products of combustion by means of a fan-blast of 7 ft. diameter through long flues, provided with ground-in bottom-slides, into a soot chamber. The slides serve to admit air as well, in order to make different qualities of soot, according to their position, for all technical purposes—such as "fat soot" for oil-cloth manufacturers, and calcined soot of all kinds for patent leather, indiarubber, and printers' ink manufacturers.

Thalwitzer (Ger. Ps. 9426 and 13691) prepares lampblack by rotating metal disks, cooled with water, over lamps fed with oil, and removing the soot formed by scrapers.

Other apparatus for the manufacture of lampblack have been described by Benoist & Camolly (Fr. P. 226418), Goulard (Ger. P. 34324), Wassermann (Ger. P. 35104), Rössler & Reinhard (Ger. P. 54201), Schlösser & Ernst (Ger. Ps. 31108 and 35942), Rösing (Amer. P. 432410), Neuninger (Ger. P. 56742), Eichfelder & Winckelmann (Ger. P. 57278), Schneider (Amer. P. 487971), Mueller (Amer. P. 492255), Wegelin (Ger. Ps. 105633, 114280, 124467, 129647, 138940, 179179, 198646, 201262, 202118); B. P. 13837, of 1903; Meiser (Ger. P. 203711). Zellner (*Die künstlichen Kohlen*, Berlin, 1903), Alfons Custodis in Düsseldorf, Zerr und Rübenkamp (*Handbuch der Farbenfabrikation*, Dresden, 1905, p. 590).

The *smoke issuing from the chimney of lampblack chambers* is rather offensive; this should be avoided by making the passage of the gases so long that at last all the soot is effectually condensed. In an English works there is a "black-house," 150 ft. long, and so divided by partitions as to cause the smoke to traverse a distance of 500 ft.; it then passes through a fire in which it is completely consumed.

The last portions of soot, before the gases issue into the air, are usually retained by coarse canvas, or by a wire sieve; but these filters are quickly stopped up and cause much trouble. This is avoided by Köhler's apparatus, shown in Fig. 162. It is a kind of Venetian blind, 3 ft. square, made of sheet-iron; the flakes of soot, on striking against this, are deflected and fall to the bottom, whilst the gases pass out without hindrance.

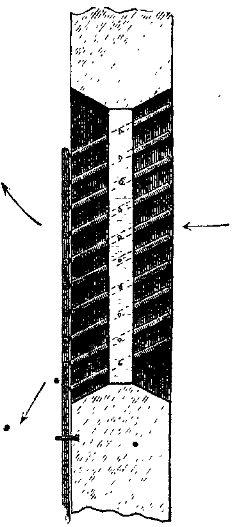

FIG. 162.

The same object is more completely attained by Siemens's "spiral deflector," Fig. 163, where the gyrating movement imparted to the gases causes the solid particles to coalesce into larger masses, which, on leaving the spiral in a tangential direction, strike against the walls of a collecting-chamber, whilst the gases escape into the chimney.

Arrangements for dealing with the gases escaping from the soot-condensing chambers are also described by Lindner (Ger. P. 47907), Dewey (B. P. 14644, of 1889; Ger. P. 51896).

The observation made by Professor Lodge, that soot or similarly finely suspended particles may be caused to subside rapidly by means of an electric current, has been followed up by Irvine and Mitchell (*J. Soc. Chem. Ind.*, 1889, p. 377), and with perfect success, but the cost of the process has so far prohibited its practical application.

Applications of Soot (*Lampblack*).—The soot, as it is removed from the chambers, is directly fit for most uses. Enormous quantities are now consumed in the manufacture of carbon electrodes; also in that of patent leather and for printers' inks. In this crude state soot contains tarry substances, which can be easily perceived by rubbing it up with a few drops of spirit of wine or benzol on a piece of white paper,

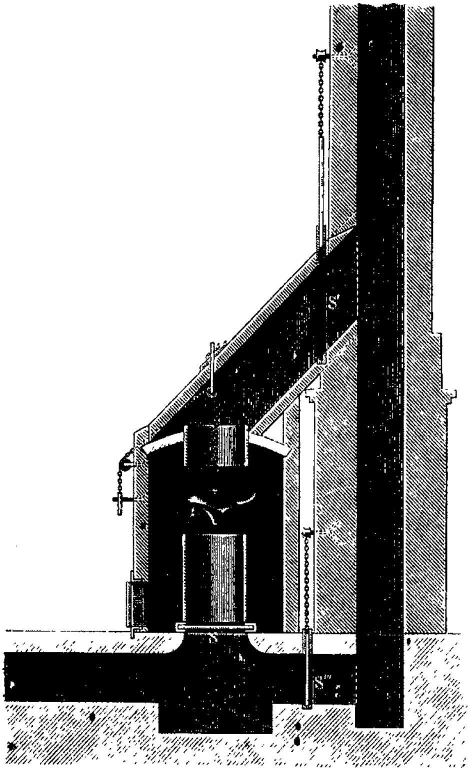

FIG. 163.

when a brown colour will be noticed on the other side of the paper.

For better printers' and lithographers' ink these empyreumatic substances must be removed, which is done by *calcining* in closed parts in a furnace, as shown in Fig. 164, about 5 × 5 ft. wide and 12 ft. high. At the bottom there is a grate (C), provided with an ash-pan (B). Above C five brick arches (D) leaves spaces (E) of 4 in. width for the passage of the fire-gases. The space above the arches is levelled by brickwork, so that twenty-four rows of cast-iron pots can be placed on it, 9 in. wide, 16 in. high, and $\frac{1}{4}$ to $\frac{3}{8}$ in. deep. Each pot is

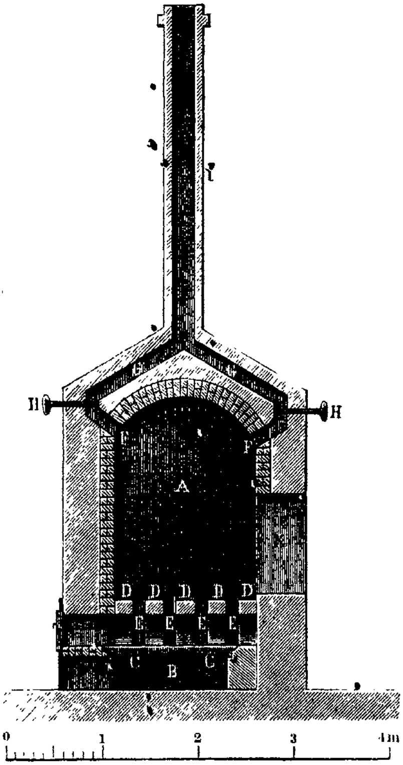

FIG. 184.

provided with a rebate round the top, into which fits the bottom of the next higher pot, only the top pot of each row having to receive a separate cover. The joints are well luted with clay. The charging-door K is bricked up during the operation. The fire-gases escape through four flues (F, F) in the four corners into a common chimney (I). The furnace is fired for eighteen to twenty-four hours till red-hot, and must then be allowed to cool down completely, as the hot calcined soot would take fire in contact with air. It forms a light, coherent mass, which is sold either as such or in the ground state.

The colouring-power of soot is all the greater the more it has been purified from tarry matters. Runge[1] examines it by mixing 1 part of soot with 2 of alcohol and 24 of gum-water (made from 2 parts of gum-arabic), taking up some of the mixture with a dry brush, weighing the brush along with the paint, and painting with it on writing-paper divided into squares. The colouring-properties of the soot correspond to the weight of the paint used and the number of the blackened squares.

Wilhelm and Bohnstadt (Ger. Ps. 12282 and 12286) make *printers' ink* by mixing 100 parts of coal-tar with 6 to 15 rosin and 10 paraffin oil, forcing through a sieve, treating with bleaching-powder to destroy the smell, and mixing with 20 to 25 parts of glycerin and 12 to 18 parts of lampblack; for the finer qualities a dark aniline colour is added. Or the tar is first heated with 2½ or 3 per cent. sulphuric acid, neutralized with soda, treated with chlorine as above, mixed with 2½ or 3 parts of lard and 4 or 5 parts of glycerin or 8 to 10 parts of soap. Sometimes they add $\frac{1}{10}$ to $\frac{2}{10}$ per cent. lampblack and logwood extract with bichromate of potash, alum, or cream of tartar.

Meurer (Ger. P. 133502) employs the soot for staining glass with a red colour. In order to prevent the loss of the soot in the glass crucible in the shape of dust, he previously mixes it with sugar syrup and moulds it by compression.

The formation of soot from tar has been utilized for protecting vineyards during cold nights against the action of frost (Russig, *Chem. Zeit.*, ii., p. 238).

Properties of Lampblack or Soot.—The average *litre-weight* of the loose soot as it comes out of the chambers, according to Zellner (*loc. cit.*, p. 55), is only 41 g.; *i.e.*, a vessel of a capacity of 100 litres would only hold 4 g. of it. It is therefore necessary to condense the soot before sending it out in bags or casks. This is in the first instance done by compressing it in the bags by hand and by the feet, and furthermore by means of suitable presses or rollers. According to Zellner the average litre-weight of soot, originally weighing 41 g. per litre, after passing once through the press or the rollers, is 236 g., after four passages 306 g., after eight passages 370 g.

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[1] *Grundriss der Chemie*, 1842, i., p. 65, on the authority of Schultz, *Steinkohlentheer*, 2nd ed., vol. i., p. 91.

Zellner (*loc. cit.*, p. 71) states the composition of six samples of soot, manufactured in various places as follows (we here quote only the extremes):—

Loss by drying, from 1·40 to 6·48 per cent.
Loss by calcining, from 0·78 to 1·83 per cent
Ashes, from 0·03 to 6·53 per cent.

Lastly we quote, from Köhler, some *statistical data* on soot, giving also only the first and the last:—

		Imported. Tons Soot.	Exported. Tons Soot.
Germany	1894	275	1200
	1910	996	3113
United States	1903	...	690
	1910	...	848

France in 1905 exported 1316 tons of soot, 94 tons of printers' ink, 109 tons of electric carbons.

Russia imported from Germany in 1903 690 tons, in 1910 844 tons of soot, mostly for the manufacture of black india-rubber galoshes.

Statistics on the Production of Creosote Oil.

We have already in Chapter I. given statistical data, comprising also the production of creosote oil for England (p. 30) and Germany (p. 35).

In this place we quote the official data on the importation and exportation of creosote oil for Germany in the following years:—

Year.	Imports. Tons.	Exports. Tons.
1903	6759·5	8596·0
1904	5607·7	12919·0
1905	7264·8	23292·2
1906	5809·8	28261·0
1907	7034·0	50802·0
1908	6856·6	68567·4
1909	9799·0	94416·7
1910	5120·5	89842·7
1911	2746	105100

CHAPTER VII

ANTHRACENE OIL

ANTHRACENE oil (green oil, green grease, red oil) consists of the highest-boiling portions of coal-tar, starting from the point at which the oils begin to separate solids again (*i.e.*, when the thermometer shows about 270° C. in the vapour), and going on to the end of the distillation. Its boiling-point is between 280° to 400° C. Its specific gravity about 1·1. Its colour is greenish-yellow when fresh, but it turns more brownish by the action of the air. At 60° C. it should be quite liquid, but when cooling down, the crude anthracene separates out in the form of greenish-yellow, sandy crystals.

Composition of Anthracene Oil.—It contains essentially the following bodies—napnthalene, methylnaphthalene, anthracene, phenanthrene, acenaphthene, diphenyl, methylanthracene, pyrene, chrysene, retene, fluorene, fluoranthene, chrysogen, benzerythrene, carbazol, acridine, hydroacridine; but along with these substances, all of which (except methylnaphthalene) are solid and partly only fuse at a high temperature, there is a mixture of liquid, high-boiling oils of which we know as yet very little.

An investigation made by E. Lehmann (Inaugural Dissertation, Munich, 1911) of the indifferent hydrocarbons of anthracene oil showed in the liquid portion, besides the substances removable as picrates, the presence of the hydrides of anthracene and phenanthrene (the di-, hexa-, deca-, and dodecahydride of anthracene, and the tetra- and octohydride of phenanthrene), also the paraffins of the formula $C_{20}H_{42}$ (eicosan), and $C_{22}H_{46}$ (decosan); the perhydrides of those hydrocarbons could not be found. Substances containing oxygen (phenols of high boiling-point) are also present; of these α and β naphthol have been distinctly proved to exist in coal-tar. The whole forms a mass rather thinner than butter, with crystalline grains or scales intermixed, of greenish-yellow colour.

The *working-up of anthracene oil* consists essentially in the separation of the solid from the liquid hydrocarbons by *cooling* and *pressing*. The latter go back to the heavy oil, of which the anthracene oil was the last fraction; or they are employed as lubricants, or are redistilled. The solid portion is either sold as crude anthracene or is further purified by "washing."

Simple as the process of making crude anthracene appears, the different ways in which it is conducted make great differences in the yields of anthracene, which, from the high price of this article, considerably affect the profits of tar-distilling.

The quantity of crystals which separate on the cooling down of anthracene oil, and which constitute the crude anthracene, is from 6 to 10 per cent. of the anthracene oil. As these crystals contain about 30 per cent. real anthracene, the latter amounts to from 2½ to 3½ per cent. of the anthracene oil.

Currie (*Chem. News*, xxxi, p. 175) asserts that a larger yield of anthracene is obtained by adding *sulphur* to the tar before distilling; a copious evolution of hydrogen takes place. It does not appear that this process is worked anywhere.

Rispler (*loc. cit.*) justly remarks that that department of a tar-distilling factory in which large quantities of crude products are worked up, in order to recover only a small quantity of final products, causes very considerable expense, with very small profits. At the present low selling prices of anthracene its recovery can only pay where it is done on a large scale, and with plant dispensing as much as possible of manual labour.

The rentability of the recovery of anthracene is also strongly influenced by the quality of the tar. Gas-tars, formed in the distillation of coal, to which a considerable addition of cannel-coal or other descriptions of paraffinoid coals had been made, yield anthracene containing paraffins which is quite unsaleable. Altogether the percentage of anthracene in the crude tar is decisive on the question whether a plant for the recovery of the anthracene will pay, or not.

Quality of Crude Anthracene.—According to Rispler, the percentage of pure in crude anthracene is greatly dependent on the origin of the tar. Pressed raw anthracene from gas-tars contain from 34 to 37 per cent. of pure anthracene; raw anthracene from coke-oven tars only 20 to 24, sometimes as little as 14 to 16 per cent., in which case the recovery of pure anthracene will not pay. The percentage of pure anthracene and the other products is shown in the following table. There is recoverable:—

100 kg. Crude Oil yield.	From Gas-tar.		From Coke-oven Tar.	
	Pressed substance	Pure Anthracene	Pressed substance.	Pure Anthracene.
Direct deposit	0·72	0·259	2·10	0·503
From the filtered anthracene oil	0·14	0·046	0·95	0·152
From the residue left behind on distilling the filtered oil	0·26	0·067	1·05	0·115
	1·12	0·372	4·10	0·770

If the market prices are tolerably good, it is possible to get out of gas-tar, containing 0·372 per cent. pure anthracene, 0·3 per cent., since the quantity of pressed substance is small and the cost of working it correspondingly low; but from coke-oven tar, containing 0·770 per cent. pure anthracene, on account of the large quantity of crystals to be worked up, only 0·4 to 0·5 per cent. It is therefore not always the best proceeding to aim at the largest possible yield of anthracene.

The percentage of pure anthracene in the crude anthracene crystals varies very much with the boiling-points of the distillate. In working up coke-oven tar and dividing the anthracene oil into numerous small fractions, Rispler obtained the following results:—

Fraction No.	Specific gravity.	Pressed substance.	Pure Anthracene in the pressed substance	Pure Anthracene in the fraction.
		per cent.	per cent.	per cent.
1	1·050	21·1	3·66	0·77
2	1·055	19·2	4·99	0·98
3	1·060	11·2	11·57	1·29
4	1·065	7·4	18·12	1·34
5	1·070	6·8	27·98	1·90
6	1·075	9·1	29·69	2·72
7	1·080	9·1	27·56	2·52
8	1·085	10·3	25·78	2·65
9	1·090	13·0	22·27	2·89
10	1·095	14·4	22·40	3·22
11	1·100	14·3	20·38	3·32
12	1·105	16·8	20·14	3·39
13	1·110	25·4	15·09	3·84
14	1·115	25·4	14·67	3·37
15	1·120	24·4	14·61	3·56
16	1·125	24·0	14·60	3·51
17	1·130	25·3	14·49	3·66

When working up a mixture of the fractions, beginning with No. 4, (sp. gr. 1·065), up to the end of the distillation, and repeatedly distilling the filtrates, the following yields were obtained:—

Fractions.	Specific gravity of the oil.	Per cent. of the tar.	Pressed substance.		Calculated percentage of pure anthracene in the oil.	Yield of pressed substance from the tar.	Yield of pure anthracene from the tar.
			Per cent. of the tar.	Contents of pure anthracene.			
				per cent		per cent	per cent.
4 to 17 . .	1·09	20·00	11·00	20·10	2·21	2·20	0·442
By distilling the filtered oil .	...	...	6·10	11·00	0·67	1·22	0·134
						3·42	0·576

On comparing the analyses of fractions 1 to 17, it is seen that fractions 4 to 12 yield a good, fractions 3 to 17 a poor pressed substance; from this, Rispler concludes that it would be advantageous in actual work to condense the anthracene oil in two fractions, corresponding to his small fractions No. 4 to 15, as "anthracene oil No. I.," and the fractions 16 and 17 as "anthracene oil No. II." These would yield the following products:—

Fractions.	Specific gravity of the oil.	Per cent. of the tar	Pressed substance.		Calculated percentage of pure anthracene in the oil.	Yield of pressed substance from the tar.	Yield of pure anthracene from the tar.
			Per cent. of the oil.	Per cent. of pure anthracene.			
Anthracene Oil I. .	1·103	17·02	10·6	21·3	2·26	1·80	0·385
Anthracene Oil II. .	1·135	2·98	25·8	14·0	3·61	0·77	0·108
						2·57	0·493

Only the anthracene oil I. should be worked for commercial anthracene, containing at least 40 per cent. pure anthracene, whilst anthracene oil II. on pressing or centrifugalling yields substances which it does not pay to work for commercial anthracene, and which should be made use of for softening the pitch or for manufacturing soot, whilst the oil filtered therefrom can be utilized as an absorbent for naphthalene, or for "carbolineum."

Most factories do not proceed in this manner, but collect the anthracene oil in a single fraction, and redistil the oil filtered from the crystals, obtaining a less valuable crude anthracene from fraction II. and filtered anthracene oil for the above-mentioned purposes.

Crystallization of Crude Anthracene.

Cooling the Anthracene Oil.—The oil is first allowed to rest for some time, so as to cool and deposit the crystallizable substances. Even in summer five to eight days should suffice; but at some works a fortnight is allowed. In any case, much anthracene remains dissolved in the liquid oils, which are therefore frequently redistilled in order to obtain more anthracene. Cooling by means of refrigerating machines hastens and completes the crystallization; but as it also renders the mother oils very viscid, artificial cooling would seem adapted only for the hot season. The cooling is best effected in shallow iron pans, not more than 18 in. deep; where space is an object, several such may be mounted one above another. It is best not to cool down to 15° C., since otherwise the crude anthracene comes out too impure.

Before pumping the crude anthracene into the cooling-pans, the water contained in it, owing to the employment of steam in the last stage of the distillation of tar, should be removed, since it gives trouble in the subsequent filtration and leaves an undesirable amount of moisture in the anthracene. The crystals deposited in the cooling-pans are usually in a muddy form if the oil was obtained from gas-tar, or in solid masses if obtained from coke-oven tar (Rispler).

Rispler points out that the ordinary cooling-pans have several drawbacks. They require a good deal of manual labour, and the men occupied with that work, owing to the action of acridine, are subject to inflammations of the skin and of the eyes, which cannot be avoided even by cleanliness on their part, so that the men working in that department must be changed at short intervals. Rispler therefore proposes a mechanical cooling apparatus (described in *Chem. Zeit.*, 1910, No. 121), consisting of tanks, provided with stirrers, served from a common driving-shaft, and charged with the hot oil directly from the condensers of the tar-stills.

Filtering.—When the crystallization is complete, the pasty mass, testing about 10 per cent. of pure anthracene, is forced by air-pressure into *filters* made of strong bagging. Even in this process there are differences; and in 1880 I found at some even very large works long rows of bag-filters of the old shape, in which the oil slowly drains off. A much better plan is the following, up to recent years frequently found in English tar-works, the apparatus forming a rough kind of filter-press. A force-pump, or compressed air, forces the paste into a 4-in. main-pipe, *a* (Fig. 140), from which branch off a number of 1-in. T-pieces, *b b*. Over their flanged end sacks, *c c*, made of strong bagging, are tied with string. The sacks are open below, but are at first tied there also. When filled, they are about 1 ft. in diameter and 4 or 5 ft. long. They hang over a tank for receiving the oil draining off. When the forcing apparatus is set in motion, the sacks are filled with the anthracene-oil paste, of which the liquid portion at once begins to drain off. This goes on slowly, as the oils are viscid; but by increasing the pressure, until the gauge shows at least 1 atmosphere over-pressure, the draining is effected much more speedily and completely, so that the contents of the sacks become nearly dry. Certainly a considerable quantity of the finer crystals is forced through the bagging along with the oils; therefore the latter must be allowed to settle, and the deposit again pressed. When, in spite of pressure, nothing more runs out, the sacks are emptied. For this purpose a small carriage, *d*, is run on a line of rails underneath each sack in turn; the lower string is untied, and the falling-out of the contents assisted by knocking the sack. The rough anthracene thus obtained usually contains 12, or at most 15 per cent. anthracene by Luck's test.

In Germany filtering-boxes are frequently employed, with laths on both the sides and bottom, about an inch apart, covered with rather densely woven jute sacking, where the crude crystals are allowed about a week for draining. The jute filters, when quite new, always allow some of the finer crystals to pass through, but after a short time the oil passes through in a clear state, certainly very slowly. The filtering-boxes are placed directly over the reservoirs for anthracene oil (generally made of wrought iron), from which the oil is forced either by pumps or by montejus into the redistilling apparatus, or into store vessels. Since it takes about a week before the anthracene has completely crystallized out of the next charge, there is sufficient time for the draining in the filtering-boxes.

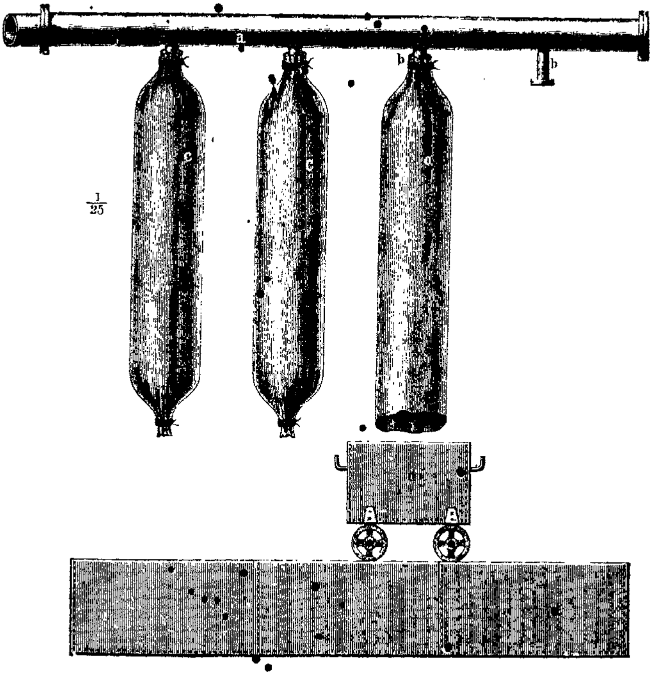

FIG. 140.

The just-described style of filtering is, of course, not adapted to the requirements of large factories. In these for a long time past *filter-presses* have been employed, of which there is a great variety of systems. We show here, in Figs. 141 and

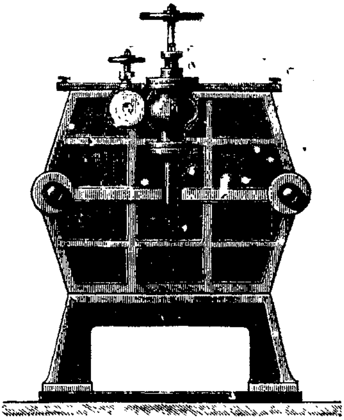

FIG. 141.

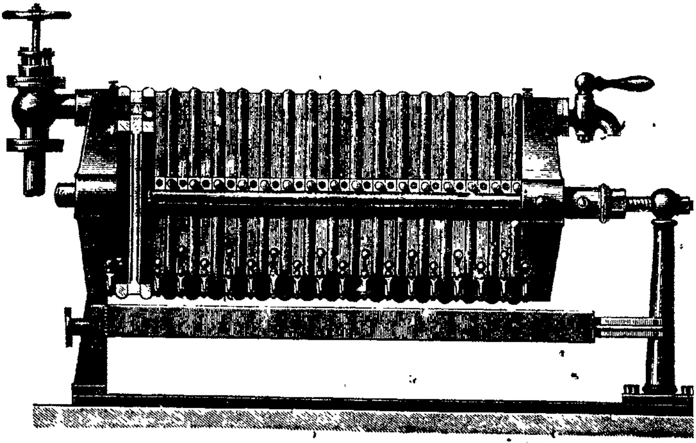

FIG. 142.

142, the press designed by Danek, and manufactured by Messrs Dehne, of Halle. We abstain from describing these presses and the way of working with them, as this is generally known, and such descriptions are always obtainable from the firms supplying the presses. The employment of filter-presses can be especially recommended for treating anthracene oils of a tough kind and yielding comparatively little crystals, *e.g.*, that obtained from gas-tar. In this case a comparatively high pressure must be applied, in order to obtain a sufficiently dry filter-press residue containing from 12 to 18 per cent. pure anthracene. After thoroughly stirring up the oil in the cooling- or crystallizing-pans, the whole contents of these is run into a forcing-boiler (preferably provided with agitating gear) and forced through the filter-press at a pressure of 2 or 3 atmospheres. When all the frames of the filter-press are filled, the last particles of oil removable in this way are forced out by compressed air, and only then the pressed cakes are taken out for further manipulation.

The cost of working the filter-presses is comparatively high, owing to the considerable amount of steam required for the pump, and of the manual labour. When working up anthracene oil from coke-oven tar, which yields much more and comparatively large-sized crystals, the employment of filter-presses cannot be recommended, since that description of oil filters much more rapidly, and the large quantity of solid masses compels emptying and recharging the press at short intervals. In this case, and nowadays in most cases altogether, the filtration takes place by means of an *aspirating-machine*. This is a box, open at the top, with a double bottom, the upper bottom being perforated with many holes and covered with a coarse filtering-cloth. The space between this and the solid bottom communicates by means of a pipe with a cylinder, generally placed below, and connected with the vacuum-pump. Great part of the oil passes through the filter without employing a vacuum, but the application of the latter hastens and completes the process. The solid residue remaining in the machine is not quite so dry as that obtained in the filter-presses, but this is not of very great importance, since nowadays it is necessary to supply the market with anthracene of at least 40 to 45 per cent., and such an article can anyhow only be produced by washing the solid residue with oil, etc.

In lieu of the open aspirating-machines, from which the pressed residue must be shovelled out by manual labour, thus causing to the attendants the "pitch-cancer" mentioned *supra*, p. 201, *closed aspirating-machines* can be employed which are provided with a tightly screwed-on cover, removed only from time to time for cleaning purposes, and with a steam-coil below the perforated bottom, which allows of dissolving the pressed residue after removal of the anthracene oil to be dissolved in the solvent required for its purification at higher temperatures, and of forcing this solution by air-pressure to the place where it is to be further treated. In the top cover there is a tap for the compressed air by which the mass can be blown out at the end of the process.

Centrifugal machines are also employed, with 1500 or 2000 revolutions per minute, especially for thicker oils. The crude anthracene is either put into sacks made of strong jute, placed close together, or, less preferably, passed directly into the drum of the centrifugal. The work is continued for about an hour. When commencing with the crude anthracene from the filters, the centrifugalled product shows 28 to 33 per cent. real anthracene. It is even possible (private communication from Dr Bueb) to obtain 70 or 80 per cent. stuff by washing the product in the centrifugal itself with solvent naphtha or other suitable liquids; but this process causes too much loss, and has been abandoned. According to the experience of Köhler, centrifugals are not suitable for treating mucilaginous anthracene oils, and require a large amount of power. Rispler points out that these machines, unless very carefully attended to, cause considerable losses of crystals, and, moreover, require frequent repairs. The centrifugals can be advantageously employed for treating the solid residues obtained by other means, and containing from 10 to 20 per cent. of anthracene oils.

Hydraulic Presses.—Many factories, in preference to centrifugals, press the preserved product in hydraulic presses, either vertical or horizontal. Vertical presses (Fig. 143) are mostly used; they are just like those employed at beetroot-sugar works. The rough anthracene is put into cloths and exposed to a gradually rising pressure, at last up to 300 atmospheres, till nothing more runs off. Sometimes, especially if the first draining has been effected in bag-filters only, the first pressing is done cold; and at one of the works visited by me it was asserted that they were getting up to 30 or 32 per cent. anthracene by mere cold pressing. But mostly that strength is only attained by *heating the oils*, to make them more liquid and to melt the naphthalene. The application of *heat* takes place in

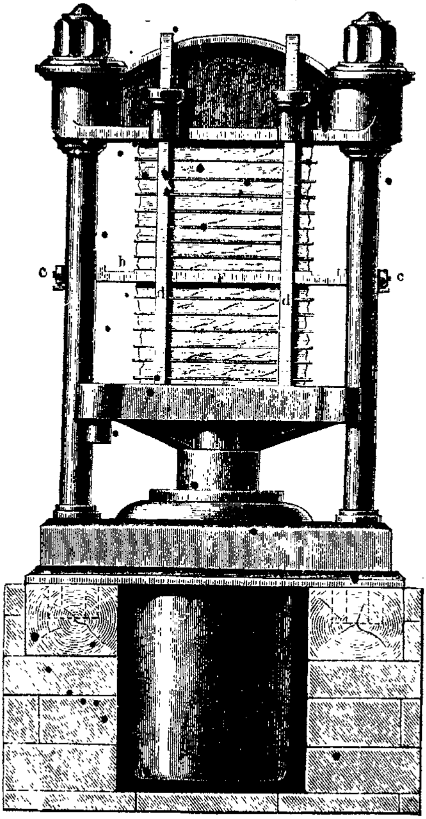

FIG. 143.

various ways. Sometimes the oil is warmed before pressing, in a pan with double bottom, by means of steam, and is then pressed in an ordinary hydraulic press. This process will hardly yield such uniform results as are obtained by real hot pressing. In summer from 35 to 36, at most 38, per cent.

anthracene is obtained, in winter sometimes near 23 to 25 per cent. At the previously mentioned German works, where they got up to 12 per cent. by filter-pressing, they got up to 32 per cent. by *cold* hydraulic pressing, and by means of a horizontal press with heated plates they attained 50 to 52 per cent., without any washing by naphtha. In England the presses are usually surrounded by a wooden jacket, and steam is passed in during this operation. This process is not very cleanly; and the redistillation of the pressed oils is made more troublesome by the admixture of liquefied steam. Far the best, although more costly to erect, are presses similar to those used in the stearine-manufacture, whose hollow plates are *heated by steam* to about 80° C. The form here shown (Fig. 144) of the horizontal shape generally used at stearine-works, is that employed at most German and Dutch tar-works. This kind of press is very efficient indeed, but it is rather troublesome to charge and discharge. Much more convenient is a press which I saw at a large English tar-works. It is a vertical press, each plate being hollow and heated by a steam-pipe joined to it by a steam-tight socket, just like the plates in the horizontal presses. Each plate is at either side provided with a pin, sliding in slanting grooves provided in the sides of the perpendicular framework. When the ram rises the plates are all raised, and are eventually subjected to as much pressure as is desired; but when the ram descends, each plate is arrested at a short distance from the next by the pins being caught and stopped, so that finally the plates appear fixed at equal intervals, leaving spaces between for introducing the cloths filled with crude anthracene.

According to Kraemer and Spilker (*Muspratt-Bunte*, viii., 67), centrifugals work best, both with respect of cheapness and of removing the oil from the crystals. A filter-press of 24 chambers and 1 square metre section, in twelve hours yields about 2 tons pressed stuff; a vacuum filter with 3 square metres filtering surface, from 2 to 3 tons; a centrifugal with a drum of 3 ft. diameter, 1½ to 2 tons. Preferably the main quantity of oil is removed by a filter-press or vacuum filter, and the remainder by a centrifugal. The quality of stuff obtained by this process is about the same as that of cold-pressed stuff, but of course inferior to the hot-pressed crude anthracene.

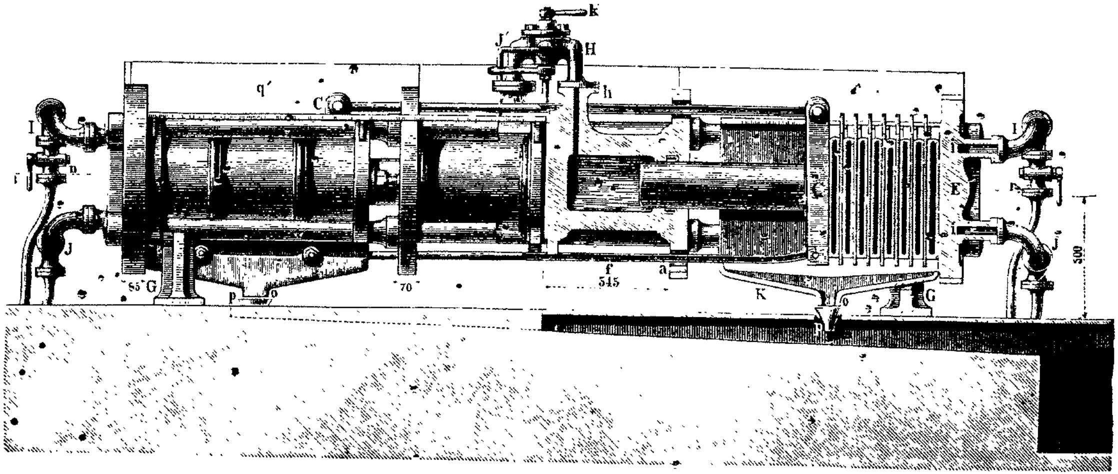

FIG. 144.

According to Köhler, hydraulic presses, both cold and hot, are nowadays but rarely employed for taking out the oils from crude anthracene. Since crude anthracene containing less than 40 per cent. pure anthracene is now almost unsaleable, tar distillers are compelled to apply further purifying operations, as will be described anon.

Scholvien (Fr. P. 335013) fuses the crude anthracene completely (at 100° C.), and cools down to 50°, whereupon the crystalline mass is drained and centrifugalled, thus obtaining directly anthracene of 45 to 50 per cent. The German patent granted for this process (Ger. P. 141359) was abandoned in 1902.

Catchpole & Catchpole (B. P. 17641, 1903) purify naphthalene and anthracene by a "sweating process," *i.e.*, by heating on a porous surface nearly to the fusing-point, viz., 70° C. for naphthalene, 200° for anthracene, in which process the less fusible impurities are removed.

Treatment of the Oils filtered from Crude Anthracene.

The oils drained from crude anthracene by centrifugals or presses are sometimes added to the creosote oil sent out for pickling wood; or else they are melted up with hard pitch in the stills in order to make soft pitch, refined tar, etc. (p. 469); sometimes they are sold at a higher price as lubricants. It is most rational to distil them over again in ordinary tar-stills, in order to recover more anthracene, which no doubt previously existed in the oils, but had been kept dissolved by the liquid components, and hence can be obtained (although but partially) only by a new fractionation. In other places the oils are only kept for several months, and the newly formed deposit is collected. E. F. R. Lucas[1] runs the tar-oil distilling between 260° and 360° (undoubtedly after separating the anthracene) through red-hot tubes filled with bricks, and distils the dark oil formed thereby; the oil distilling at 360° is rough anthracene. Almost the same proposal has been again patented by Hardman and Wischin (No. 4517, 7th November 1878), who substitute coke for bricks. At the present time processes of this kind have very little chance of financial success (*cf.* pp. 185 *et seq.*).

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[1] English patent, 24th January 1874.

A. M. Graham[1] describes the following process as the most suitable from practical experience on the large scale for extracting the anthracene from the filtered oils, which are frequently allowed to accumulate to an inconvenient extent, because the anthracene obtained from them is generally so impure as to be unsaleable. Fractional distillation, retaining only that portion of the distillate which comes over between 300° and 360°, is difficult and expensive. He prefers distilling, say, 1500 gall. of the filtered oils in a perfectly clean tar-still, free from tar and pitch, until crystals of anthracene begin to appear in the distillate on cooling. The distillation is then stopped; and after the temperature of the remainder has been sufficiently reduced, it is run out into a tank and allowed to cool, when the anthracene crystallizes out in large quantity. A second and a third operation can be performed in this way; but usually it is found that the oil is sufficiently exhausted in one operation. The solid portion deposited in the tank will be found, after filtering and pressing, to contain at least 17 per cent. of real anthracene; and this can be easily raised to 36 per cent. by fractional distillation or by washing.

Watson Smith (priv. comm.) was able to recover from the pressed oils, after treating them, while hot, with a little concentrated sulphuric acid and caustic alkali, a large quantity of anthracene by repeated distillations. The last oil boiled at 260° to 290°; the fraction distilling between 260° and 280° remained quite colourless after long standing; it had a pleasant hay-like smell, and the sp. gr. 1·04. It is miscible with paraffin oil and animal oils, and dissolves a considerable amount of tallow. It is also by itself a good lubricant. He could also isolate 0·28 to 0·45 per cent. crude anthracene cake from ordinary creosote oil, sold for pickling; even in the light oil, traces of anthracene were found.

Boleg[2] distils anthracene oil under a pressure of 4 or 5 atmospheres, which procedure yields a bright yellow and mild-smelling oil, much preferable to ordinary anthracene oil. This process also admits of obtaining more anthracene, as well as chrysene and pyrene. When working at 10 or 12 atmospheres, benzol can also be obtained, but this would not pay at the present prices. The pitch remaining behind can be used in the ordinary way. The apparatus (Fig. 145) shows a retort, A, of various shape and size, heated by a steam-jacket or an open fire, or, preferably, as shown here, by Th. & A. Frederking's system of superheated steam (Ger. P. 63315). B is an automatic valve, regulated so as to allow the vapours to pass over to the condensers at a certain pressure. C is a preliminary cooler with a water-jet, by which the danger of explosion or fire is minimized.

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[1] *Chem. News*, xxxiii., pp. 99, 168.

[2] *Chem. Rev. Fett- u. Harzindustrie*, 1898, pp. 94 and 97.

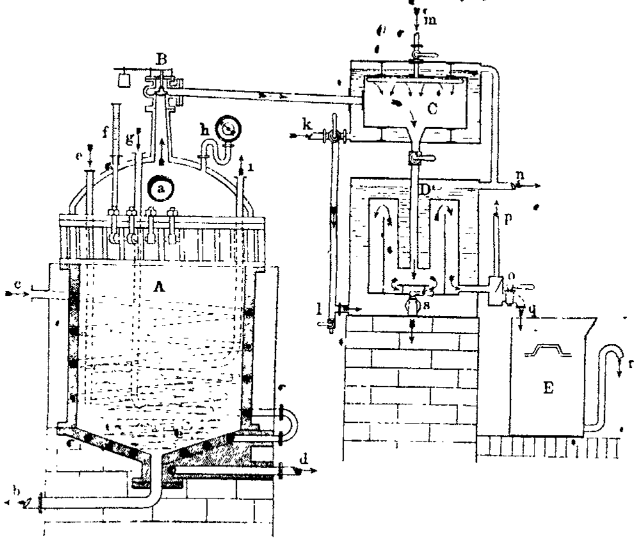

FIG. 145.

D condenser, E a Florentine flask for separating the water and oil. The retort A contains a feed-pipe *a*, running-off pipe *b*, steam-coil *c d* (cast into the sides of the vessel), perforated steam-coil *e* for open steam, inside coil *g i* for indirect steam, *f* thermometer or pyrometer, *h* and *l* pipes for cooling-water, *m* ditto for the preliminary cooler, *n* waste-pipe for cooling water, *o p* waste-pipe for gases, *q* tap for the lighter oils continually fractionated in the condenser, *s* pipe for the heavy oils, *r* waste-pipe for condensed water.

The retort is two-thirds filled, the valve B is regulated for the desired pressure, and the heating is commenced by means of the steam-coils *c d* and *g i*, or one of these. At first ordinary steam of 6 or 7 atmospheres is used, afterwards superheated steam. If open steam from *e* is to be used, it must be superheated to the temperature of the retort; but this should not be done before the contents of the retort are quietly boiling.

H. Günther (Ger. Ps. 9566 and 11930) employs the filtered anthracene oil for manufacturing *black printers' ink*. It is for this purpose boiled with 10 per cent. of cupric chloride, which imparts a blackish-brown colour to it. The varnish is composed of 40 parts pitch or asphalt, 28 rectified oil of turpentine, 2 aniline violet, and 24 coal-tar oil.

The Rütgerswerke make anthracene oil *inodorous* by two methods: first, mixing with oxides or hydroxides, or salts of heavy metals, adding an alkali, heating up, and passing steam through the mixture for a certain time; second, mixing the oil with formaldehyde or acetone, or preferably a mixture of both, heating, and passing steam through for some time. We shall give details of their processes in Chapter VIII.

Carbolineum.

This name was given to heavy coal-tar oils, used for the preserving of timber, by Avenarius, who for this purpose treated anthracene oils by gently heating, agitating, and passing in chlorine gas, which is to deprive them also of their unpleasant smell (Ger. P. 46021). This special product is known as "Carbolineum Avenarius" or "Avenarine," but the name of "carbolineum" is given in Germany to many other coal-tar oils or preparations serving for the same purpose, since the original article has been found to be very useful indeed for this purpose.

Some of these oils are of much lower specific gravity, and really belong to the "creosote oil," to be treated in Chapter VIII. Filsinger (*Chem. Zeit.*, 1891, 544) reports upon some of the "carbolineums" of trade, whose specific gravity, with one exception, was between 1·046 and 1·108, and which ought not to have gone under that name. According to Hodurek (*Oesterr. Chem. Zeit.*, 1904, No. 16) good carbolineum should have a specific gravity not below 1·120; it should not begin to distil below 230° C.; its inflaming-point should be above 120° C.; its viscosity should be as great as possible, its colour red-brown and it should not contain any solid matter crystallizing out. Sometimes ordinary green anthracene oil is purposely coloured red-brown, to resemble real carbolineum, by adding colouring matters, or filtered tar or pitch. Timber soaked with real carbolineum retains its nut-brown colour for a long time, but timber treated with oils containing tar or pitch soon get darker.

Hodurek believes that the treatment with chlorine, prescribed by the Avenarius patent, is both useless and inefficient. He found as much chlorine in the original oil (0·18 per cent.) as in Carbolineum Avenarius (0·16 per cent.), and in both oils the aqueous extract showed just the quantity of NH_3 corresponding to the Cl present. The proportion of acids (phenols) in good carbolineum amounts to 10 per cent. against 5 to 7 per cent. in ordinary anthracene oil. According to him, all the above-mentioned good qualities can be imparted to coal-tar oils without the application of any patented process, by simply applying a suitable fractionation during the distillation of the tar.

Recently there is found in the German trade an article, sold as "Inodorous antinonnin-carbolineum," which consists of potassium dinitro-cresylate.

Graf & Co. (Ger. P. 63218) make similar oils by treating wood-tar or coal-tar oils with ozonized oxygen or air.

Herborn (B. P. 3922, 1901) obtains a product equal to the "Carbolineum Avenarius" by shaking up anthracene oil with 3 per cent. hydrochloric acid and 2 per cent. of a saturated aqueous solution of zinc chloride. The product is reddish-brown, without smell, and contains 2 per cent. chlorine.

The article sold as "argon" seems to be identical with carbolineum. "Barol" is carbolineum containing some copper compound. "Phenola" is another name for it.

Emma Homann (Ger. P. 154034) employs Carbolineum Avenarius + 2 per cent. soft soap + 1 per cent. cupric sulphate as a protection for trees against "tree-cancer" and the ravages caused by animals.

Knoll & Co. (Ger. P. 175384) obtain permanently liquid high-boiling coal-tar oils by the addition of high-boiling distillates from juniper tar or other wood-tar, or distillations of bituminous masses, like ichthyol oils.

Hübsch reports in a Silesian paper that a human body which had been buried in a coffin impregnated with carbolineum, on being exhumed after two years, was found to be altogether mummified.

Nördlinger (*Pharm. Zeit.*, 1907, p. 1097) tests carbolineum and similar oils by absorbing them in scraps of porous paper, estimating the loss of weight by volatilization of the lighter oils and extracting the residue with ether.

G. Blass and Sohn (Ger. P. 177249) employ anthracene residues for converting liquid tar into a solid mass.

Bokorny (*Bitumen*, 1911, p. 349) discusses the action of carbolineum on vegetation. It does good service for treating injured trees and shrubs, as protective paint against shield-lice, etc.; also for disinfecting the soil. According to Hiltner, it essentially promotes the fertility of the soil, but according to Molz (*Bakt. Zentr.*, 30th May 1911) it does so only if put in the soil several months before sowing, whilst it is injurious if the disinfection takes place immediately before putting in the seed. Molz states that "soluble carbolineum" (solutions of tar-oil soaps) in 10 or 20 per cent. solutions frequently acts very well against shield- and blood-lice, caterpillars, tree-cancer, peronospora, mould, bacteria, etc. For destroying the weeds in vineyards the raw tar-oils or raw phenols do very good service. The sensitiveness of the leaves of plants against carbolineum solution (10 per cent.) differs very much; the leaves of apple-, pear-, plum-, peach-, gooseberry-, currant-trees are very sensitive to it.

The testing of carbolineum will be described at the close of this chapter.

Employment of Anthracene Oil for removing Naphthalene.

An important use of anthracene oil is that for *removing the naphthalene from illuminating gas* (Bueb's process), and thus preventing the stopping-up of gas-pipes by naphthalene crystallizing in them (*J. Gasbeleucht.*, 1902, pp. 516, 872; 1903, p. 45). The oils are most suitable for this purpose when cooled down, and the less distillates up to 270° C. they contain. Thus anthracene oil of sp. gr. 1·11, according to Hodurek (*Oesterr. Chem. Zeit.*, 1904, No. 16), at 28° C. dissolved 22½ per cent. of naphthalene, but when from the same oil the oils distilling up to 270° were removed, this distillate dissolved only 3 per cent. naphthalene (oils from lignite tar dissolve up to 33 per cent. naphthalene).

Since the anthracene oil used in Bueb's process would take out of the gas some of the benzol vapour, so important for its illuminating power, it is now usual to add to the anthracene oil used for washing the gas, 4 per cent. benzol. In this case the gas passing through the washer neither gives up nor takes up benzol from the washing oil at the proper temperature. The firm Röpert in Dessau sells by the name of "Röpertöl" oil corresponding to Bueb's description, of two kinds (with or without benzol).

Ellery (*J. Gas Lighting*, 1910) has found the following data for the absorption of naphthalene at 0°.

	Per cent.
Benzol	24·90
Tar oil (? quality)	9·74
Creosote oil	3·15
American gas-oil	5·89
Oil-gas tar	23·50

The strong action of oil-gas tar shows that this tar must do good service for removing the naphthalene from coal-gas and water-gas. In fact Gill (*J. Gasbeleucht.*, 1910, p. 1097), on passing coal-gas through a scrubber, fitted with coke and fed with water-gas tar, removed the naphthalene from the gas down to 0·6 to 1·6 g. in 100 cb.m.

Bayer (*ibid.*, 1911, p. 496) gives his results on the action of various tar-oil fractions in this way.

Tar-oils used in the Construction of Basic Linings in Steel Works.

J. Wagner (*Rev metall.*, 1914, xi., p. 211) compacted powdered dolomite with each of several fractions obtained in the distillation of coal-tar, heated the mixtures at 700°, and determined their strength in compression. From his experiments he drew the following conclusions as to the *useful* constituents of the tar: (1) The acid oils (creosote oils) are useful, because their fluidity facilitates intimate mixture, their acidity causes disintegration of the dolomite, and their decomposition furnishes carbon for cementation; (2 and 3) the anthracene oils and the heavier products which leave a large residue of carbon.

The *harmful* constituents of tar are as follows: (1) the light oils which in volatilizing without decomposition may carry off useful substances; (2) the naphthalene which prevents penetration of the useful bodies; (3) carbon in too great quantity; (4) organic bases which neutralize the acids. He recommends carrying out the distillation *in vacuo* to completely remove the naphthalene at a low temperature.

Purification of the Pressed Anthracene by Washing.

Formerly at most works the anthracene turned out by hot-pressing only came up to about 30 to 33 per cent. in winter, and 33 to 36 per cent. in summer. In 1908, the crude anthracene was sold in Germany at 40 per cent., to which point it would appear it can now be brought without any difficulty. At one German works I was credibly informed that they got up to 50 or even 52 per cent. without any washing with naphtha, by three successive pressings, namely, 12 per cent. by the filter-press, 32 per cent. by the cold hydraulic press, and 50 to 52 per cent. by the horizontal steam-heated press (*supra*, p. 600).

Such work, however, is decidedly exceptional, and can be explained only by differences in the fractionation during the distillation of the tar. The great majority of tar-works obtain such rich anthracene only by *washing, i.e.*, treating with solvents of the impurities. As such, carbon disulphide and alcohol have been thought of, but have hardly ever been used, on account of their cost, their volatility, and the danger of fire. The reagent used in most places is the *solvent naphtha* which is obtained on rectifying the light tar-oils, and essentially consists of xylenes, pseudocumene, and mesitylene. It distils between 120° and 190°, as we shall see in detail in Chapter X. In this naphtha, especially phenanthrene, is much more soluble than anthracene, but the carbazol (of which there is about 14 to 18 per cent. present) is not removed, but remains behind with the anthracene. In England, petroleum spirit of not more than 90° boiling-point is frequently used; that boiling at 100° dissolves too much anthracene. Creosote oil is also sometimes employed, as we shall see.

Before washing, the rough anthracene cake should be ground up into fine powder, which must also be done if it goes directly into the trade. The grinding is effected by any sort of machine such as horizontal mills, edge-runners, studded rollers, Carr's disintegrators, etc.. The powder produced is usually stirred up during several hours with the naphtha in closed iron boilers, vertical or horizontal, fitted with a mechanical agitator and with a steam-jacket or an interior steam-coil. This is done for several hours, gentle heat being applied; and the whole is then forced by compressed air into a filter, consisting of an iron box with an inner perforated false bottom, covered with canvas, where the solution is separated from the solid parts, the separation being greatly facilitated by the air-pressure. To avoid danger of fire, the filters, the tanks for receiving the oils, etc., must not communicate with the outer air. It would seem advisable to employ an arrangement sketched in Fig. 146: *a* is the dissolving-boiler with its agitator; *b*, the filter, with the manhole *c* for removing the anthracene; *d*, the vessel for receiving the solution of the impurities in naphtha; *e*, an air-pump, aspirating the air from *d* and forcing it into *a*. Thus the whole of the paste is forced through the pipe *f* into the filter *b*, and the solution through it into *d*. In this way the same quantity of air is always circulating, and a loss of naphtha is avoided as much as possible. Or else the mass may be treated in a centrifugal machine.

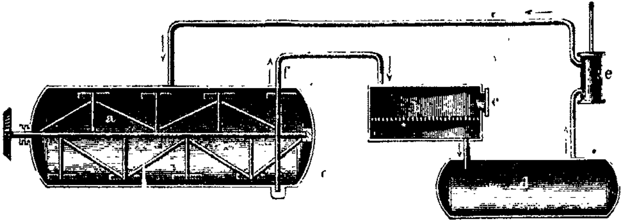

FIG. 146.

The *once-used naphtha* is always recovered, except the inevitable loss, by distilling the solution. The *residue* remaining in the still—consisting mainly of phenanthrene, along with some anthracene, methylanthracene, naphthalene, phenol, and unknown liquid lubricating-oils—is mostly not used for anything except burning to make lampblack (p. 373), for which it is very suitable; but care should be taken that no water remains mixed with it. From this residue, as well as from other products of coal-tar distillation, *pure phenanthrene* might be produced in large quantities, if this substance should ever become the starting-point for other useful products; at the present time it has practically no commercial value. We come back to this point at the end of this chapter.

Some anthracene-refiners recover, by fractional crystallization, the anthracene, of which there is sometimes as much as 8 per cent. in these residues; but the majority seem to think this process too expensive, especially as this anthracene is always contaminated with methylanthracene.

The washing-process employed at one of the largest English tar-works is as follows:—The hot-pressed anthracene is ground up, and is well-mixed in a closed machine with hot solvent naphtha, at a temperature of 77° C. The mixture is allowed to cool down to 21° C., and is now submitted to strong hydraulic pressing. In order to avoid escapes and danger of fire, the press is enclosed in a casing. The press-cakes are heated in a 3-ton still up to the melting-point of anthracene, the vapours being condensed in a small worm; and the melted anthracene is run out and solidified in iron boxes. The solution running out of the hydraulic presses is distilled in ordinary light-oil stills, and the distilled naphtha is used over again for washing anthracene. The residue remaining in the still is first treated for the extraction of some anthracene, by a process said to be very simple, and is then either burned or worked into the creosote oil or the pitch.

The washing with naphtha yields a product of at least 45 or 50 per cent. real anthracene, and with proper care upwards of 50 per cent.; the highest amount formerly obtained was 70 per cent., and refers to the above-mentioned article that had been previously brought to 50 per cent. by three pressings. Some manufacturers, during recent years, have got up to 80 or even 85 per cent., but mostly without commercial success. Later on methods have been worked out for attaining that strength in a better way (see below). On the other hand, some makers only get at most 30 or 40 per cent., by treating the rough anthracene, merely purified in the centrifugal machine or filter-press, with naphtha and then submitting it to hydraulic pressure. Hence the former process seems more rational than the latter.

At one of the largest English works they wash first with *crude solvent naphtha* (*i.e.*, the second distillate of the light-oil still). As much as 56 or 60 per cent. anthracene is said to be obtained in this way.

Perkin[1] prefers washing with *petroleum-spirit*, boiling between 70° and 100° C., which dissolves less anthracene than coal-tar oils, and yet removes the impurities sufficiently. Coal-naphtha sometimes dissolves 7 or 8 per cent. by weight of anthracene, which is difficult to recover. The following table shows the solubilities of anthracene and some other bodies in petroleum spirit and benzol:—

	Petroleum spirit, B.p. 70 to 100°.	Benzol. B.p. 80° to 100°.
Anthracene	0·115	0·967 per cent.
Phenanthrene	3·206	21·94 „ „
Carbazol	0·016	0·51 „ „
Dichloranthracene	0·137	0·62 „ „
Anthraquinone	0·013	0·166 „ „

Creosote oil is also employed for washing anthracene. Some believe that it is not a proper reagent for this purpose, as it dissolves more anthracene than phenanthrene, etc.; but this must be erroneous, at all events with proper manipulation, since several tar-distillers employ creosote oil with great advantage, and some even believe this to be a valuable secret. In this way 40 per cent. anthracene can be obtained by the following process, which I have seen used with great success:—The first crude crystals, testing, say, 10 per cent. pure anthracene, after draining, are mixed with an excess of creosote oil at a temperature of 80°. The mixing being quite complete, the mass is allowed to cool down to 40°, and the crystals then obtained are subjected to hot pressure, when they will yield 40 per cent. anthracene, the creosote oil having dissolved far more of the impurities than of real anthracene. The tepid mother liquor is allowed to cool down to 25°, and thus a second crop of poorer anthracene crystals is obtained; and a third quality is got by allowing the second mother liquor to cool down to the ordinary temperature. The second product is put into the still, where the press-oil is distilled once more; the third product is treated together with fresh crude 10-per-cent. anthracene.

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[1] *Wagner's Jahresber.*, 1879, p. 1068.

At a large tar-works this process is managed as follows:—1200 kg. of tar-anthracene (got direct from the anthracene oil), and 600 kg. of "oil-anthracene" (obtained by redistilling anthracene oil), both of them cold-pressed, are mixed in a mechanical mixer, provided with a steam-coil, with 1000 kg. of creosote oil, free from naphthalene (the first eighth in the distillation of the tar). The mixture is first heated to 80° C., and is then allowed to cool down to 40° or 35°, according to the season. From the mixer the paste runs on to open vacuum-filters, placed on a wrought-iron boiler, evacuated by means of a Körting's injector. The contents of the filter are put into sacks and pressed cold at 80 atmospheres' pressure; the residue is immersed with the sacks in water of 50° C. slowly heated to 75°, then at once brought back into the press and pressed at 200 atmospheres, renewing this pressure twice or three times. Thus the oil-anthracene, which contains much methylanthracene, yields the latter almost completely to the solvent, and the result is very pure anthracene of 40 or 45 per cent.

At another tar-works the process is as follows:—The rough anthracene is first passed through a filter-press, and then through a hydraulic press enclosed in a steam-casing. It is now washed with creosote oil in a steam-jacketed pan, with very well-designed horizontal agitating-gear, which thoroughly mixes up the warm liquid with the crystals. The mass is now filtered by means of a vacuum, the same air continuously circulating, as I had already proposed in 1880. The anthracene thus gets up to 45 per cent.

The German tar distillers do not any more employ the just-described processes on account of the great complication and corresponding expense. The principle is always the same, but the hydraulic pressure is avoided. The product coming from the filter-presses or vacuum-presses, which still contains oily matters, is either centrifugalled and then washed with the purifying oil, or it is directly treated with the latter. The washing-oil is either "solvent-naphtha" (*vide* Chapter X.), or the oil between 170° and 200° obtained in the redistillation of light oil, or the "naphthaline oil" draining from the naphthalene, as we shall see later on.

Rispler (*loc. cit.*) describes the process as it is carried out in practice in two modifications. In the first the crude anthracene, taken out of the cooler for anthracene oil, is pumped through a filter and centrifugalled, and is then dissolved in the purifying-oil in a vessel provided with a steam-jacket and agitating-gear. The solution obtained is cooled down to 40° in a vessel provided with a water-cooling mantle and agitating-gear, whereby most of the anthracene separates out, whilst a great portion of the impurities remain in solution. The anthracene is run into a heated aspirating-filter, and then centrifugalled or put through a heated hydraulic press; the oil passing through the filter, on cooling down, separates some anthracene which is brought up to 40 per cent. in the manner described. On the average the crude anthracene obtained in this way has 47 per cent. in the case of gas-tar, or 42 per cent. in that of coke-oven tar.

The other process mentioned by Rispler is carried out in the same apparatus, but the centrifugalling is left out, and the oil for washing is that which drains from naphthalene ("creosote oil," *vide infra*), in the proportion of 20 parts to 80 parts of the crude anthracene coming from the aspirating-filter.

It is especially contended that the washing with creosote oil removes that most disagreeable impurity in anthracene, viz., *paraffin*, which differs from ordinary paraffin by fusing at a much higher temperature, and is little soluble in either petroleum spirit or naphtha. Even a little of it suffices for disturbing the filtrations necessary in the subsequent operations; it resists pretty completely all the chemical processes to which anthracene and anthraquinone are subjected, and as it melts during the process of oxidizing the anthracene to anthraquinone, it is very troublesome. It is stated that the paraffins can be removed by dissolving the crude anthracene in a steam-jacketed vessel in 1·2 parts by weight of creosote oil distilling between 220° and 330°, and previously freed from phenols by washing with caustic soda. The solution is stirred till cold, the cooling being promoted by a stream of water, and the magma is pressed in a filter-press. The anthracene thus gets up from 28 to 36 or 40 per cent. by Luck's test; but it is often *not* quite free from paraffin.

Washing with Paraffin Oil or with Oleic Acid.—C. Caspers (B. P., 9th May. 1873) proposes the following purifying process:—Well-pressed anthracene cake is mixed at from 12° to 15°. C. with its own weight of *paraffin oil*, which dissolves naphthalene, phenol, cresol, etc. The residue is washed several times with paraffin oil (always at or below 15°), and ultimately with methylated spirit, pressed, and dried at 100°. The product is said to contain 85 or 90 per cent. of anthracene fusing at 190°. This can be further purified by fusing and heating to 205°, when a dark green crystalline mass is formed, containing 95 to 97 per cent. anthracene, and yielding perfectly pure anthracene by sublimation (?). If the crude anthracene contains higher-fusing bodies, as pyrene, chrysene, etc., the washing with paraffin oil is conducted at such a temperature that the anthracene is dissolved, whilst chrysene, etc., remain behind; on cooling the clear solution down to 15°, the anthracene separates and is purified as above. (I am not certain that this process has been adopted anywhere.)

Remy and Erhart (Ger. P. No. 38417) stir 100 parts crude anthracene with 150 *oleic acid*, heated to 100° or 200°, until almost entirely dissolved. On cooling, the anthracene crystallizes almost pure, and is separated from the adhering fatty oil, first by filtering, etc., afterwards by saponifying the oil with alkali or washing with petroleum.

Washing the Crude Anthracene with Pyridine Bases.—The Chemische Fabriks Aktien-Gesellschaft at Hamburg (Ger. P. No. 42053) obtains almost pure anthracene, especially free from carbazol (which resists the other solvents), by washing the crude anthracene with the mixture of *pyridine bases* obtained in purifying light coal-tar oil, in which a certain proportion of benzol will do no harm. One part of crude stuff is treated on a steam-jacketed mixer with 1½ or 2 parts of the basic mixture and allowed to cool and crystallize. In lieu of pyridine bases, the higher-boiling aniline and quinoline bases may be employed, diluted with the same volume of solvent naphtha. Crude anthracene of 33 per cent. yields with pyridine bases an article of 80 per cent., or with aniline and solvent naphtha 75 per cent. The advantage of the pyridine as solvent is principally this: that it removes the carbazol, whereas benzol and naphtha leave this with the anthracene and remove mainly only phenanthrene. At ordinary temperatures 100 parts of benzol and its congeners dissolve 1 to 1·5 anthracene, 1 to 2 carbazol, and 30 to 35 phenanthrene. By means of these solvents no higher strength than 50 to 60 per cent. real anthracene can be obtained, and the carbazol must, if necessary, be removed by subliming or distilling over caustic potash, which is a very troublesome operation and carried out only at some colour-works (*cf.* p. 618). But the pyridine bases at ordinary temperatures dissolve 2·3 per cent. anthracene, and 22·0 per cent. carbazol, and 35 per cent. phenanthrene. Thanks to this behaviour, by recrystalling normal, well-pressed anthracene with one and a half times its weight of pyridine bases, we obtain anthracene testing upwards of 80 per cent. The apparatus for this object consists of iron cylinders, horizontal or vertical, provided with agitating-gear, holding a few tons each, heatable by a steam-jacket or steam-coil. After the solution has been effected, the liquor is cooled, with continuous agitation by running cold water through the jacket. The crystallized mass is removed from the mother liquor by a vacuum filter, and the last remainder of the pyridine mechanically kept back is removed in a steam-heated drying oven. Thus a greenish powder of distinctly crystalline appearance is obtained. From the mother liquor the pyridine is recovered by distillation. The residue left behind is an excellent material for the recovery of *carbazol* and *phenanthrene*, which up to the present are not saleable in quantity. This also holds good of *acenaphthlene* and *fluorene*, which appear in the first runnings when distilling phenanthrene, and of *chrysene* and *pyrene*, which can be got from the residue in the distillation of the first anthracene oil, or by the distillation of pitch (p. 260).

It would appear from Kraemer and Spilker's description in *Muspratt-Bunte*, viii., 68, that this process is carried out on a large scale in some German tar-works, but according to a communication from Dr Kraemer, chrysene (let alone pyrene) has never been obtained in this manner.

Various Agents for washing the Crude Anthracene.—The Farbenfabriken vorm. Friedr. Bayer & Co. (Ger. P. No. 68474) employ liquid *sulphur dioxide*, which dissolves the impurities of crude anthracene, but very little of the anthracene itself. 600 kg. crude anthracene is mixed in a wrought-iron agitator with 2400 kg. SO_2, first exhausting the air and then allowing the liquid SO_2 to enter. The reaction having ceased, the mass is forced by its own vapour-pressure into an iron, steam-jacketed, filtering-tower, where anthracene of 70 or 80 per cent. remains behind. The mother liquid is distilled, the SO_2 being collected and recondensed by means of an air-compressor.

Another patent of the same firm (Ger. P. No. 78861) recommends *acetone* as purifying agent. 560 kg. crude anthracene is stirred in a steam-jacketed cylinder with 750 kg. acetone or an analogous substance, for an hour at 60° C. After cooling, the separated anthracene is filtered and washed with 375 kg. acetone. The second liquor is used over again, the first is distilled to recover the acetone. From crude anthracene of 34 or 35 per cent. an article of 82 per cent. is easily made, and only a few per cent. of anthracene remains in the residue after distilling the acetone.

Wilton (B. P. 27559, 1898; Ger. P. 113291, abandoned in 1904) purifies rough anthracene by *liquid ammonia* (anhydrous), which dissolves out most of the impurities and leaves the anthracene behind.

The Aktien-Gesellschaft für Teer- und Erdöl-Industrie (Ger. P. 111359) purify crude anthracene in the following manner:—Most of the phenanthrene is removed by fusion and fractional crystallization; then carbazol is removed by treatment with 50 per cent. solution of caustic potash at not above 260°, and the remainder of the phenanthrene is eventually dissolved out by means of 90 per cent. benzol. Thus anthracene testing 90 per cent. is obtained as a brownish powder. This patent was abandoned in 1902.

Luyten and Blumer (Ger. P. 141186) treat drained, oily, rough anthracene without pressing, directly with a volatile solvent, filter, wash, and dry. They assert that thus purer anthracene is obtained than by the treatment of pressed anthracene, the mixture of the volatile solvent with the high-boiling oils which accompany the anthracene being particularly adapted to the purification of the anthracene.

E. Wirth (Ger. P. 122822; Fr. P. 302998) suspends the crude anthracene in benzol and treats it with nitrous acid, which, under the conditions chosen, does not act on anthracene, but transforms carbazol, etc., into nitrosocarbazols, which are separated from the anthracene with the solvent. The nitrous acid is recovered from the nitrosocarbazol by means of sulphuric acid, thus obtaining a technically useful oxide of carbazol.

Vesely and Votocek (B. P. 27596, 1904; Ger. P. 164508) heat a solution of crude anthracene in a solvent immiscible with sulphuric acid, with concentrated sulphuric acid (which acts also upon carbazol), *e.g.*, 100 parts crude (35 per cent.) anthracene (containing 12·8 per cent. carbazol), 300 solvent naphtha, and 100 sulphuric acid. The heating is continued with agitation for a few minutes, the acid is drawn off, the solution is freed from acid by agitation with calcium carbonate, filtered, and allowed to crystallize. Thus anthracene of 84 per cent. is obtained, with only 1 per cent. carbazol, and by once recrystallizing from benzol it is brought to 95 per cent.

Scholvien's patents (Belg. P. 177419; Fr. P. 335013) are almost identical with the above-mentioned Ger. P. 111359.

Owing to the great danger of fire, the washing of anthracene and the recovery of the naphtha ought to be performed at some distance from the other buildings, and not in very large apparatus.

The purification of anthracene by washing is frequently carried out, not at the tar-works, but by special anthracene-refiners or at the alizarin-works. The latter does not seem very rational—first, because this operation is much more in the style of tar-distilling than in that of colour-making, involving as it does the danger of contamination and of fire for those expensive products; secondly, because the tar-distiller can manufacture and recover the naphtha more cheaply than the colour-manufacturer.

Purifying Anthracene by fusing with Caustic Potash.—A peculiar anthracene-purifying process was employed for some time at Perkin's alizarin-works, and communicated, under the obligation of secrecy, to one of the largest German works. The secret was kept for years, even after the process had been proved to be unsuitable and had been discontinued. It is now known of what it consisted.[1] Anthracene is mixed with *caustic*

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[1] Auerbach, *Das Anthracen*, 2nd ed., p. 11; Perkin, *loc. cit.; Fischer's Jahresber.*, 1885, p. 467.

potash and a little lime, and is distilled out of cast-iron gas-retorts, or wrought-iron retorts, 4 ft. wide by 7 ft. long, heated by flues below the bottom and along the side, and protected at the bottom against the direct action of the fire by fireclay slabs. These are connected by iron elbow-tubes with shallow iron boxes, in which the distilling anthracene condenses without further cooling. The covers of these boxes are put on loosely, so that the gases evolved at the same time can escape and may even take fire without doing any harm. Caustic soda cannot be employed, because its fusing-point is too high; and as that of caustic potash is too low, quicklime is added. Two hundred kg. of anthracene are ground up with 60 kg. Montreal potash and 12 kg. quicklime, during which operation the smell of ammonia is often perceived. The mixture is distilled at a low red heat. When this mass is diluted with water, a green solution is obtained which deposits greenish-blue flocks of extremely disagreeable odour. After the distillation the retort contains a porous, wax-like substance which takes fire on contact with air and deposits a sublimate of carbazol in the cooler parts. In fact carbazol was discovered by Graebe and Glaser in this manner, and does not seem to be easily obtainable in any other way. The distillate from the retorts forms solid yellow pieces, containing about 40 per cent. real anthracene. From the residue in the retorts the caustic potash can be recovered by dilution with water and boiling with lime, or the residue is calcined, and used over again as crude potash; but unless a flue-dust chamber is interposed between the grate and the chimney, a great deal of potash is carried away by the draught as fine dust. The distillation with caustic potash is said to destroy the chrysene; but the destruction seems to extend to the anthracene, as shown by the following figures:—600 kg. of 31 per cent. anthracene cake were distilled with 180 kg. caustic potash and 36 kg. lime; the result was 380 kg. 44 per cent. anthracene, equal to a loss of 17½ kg., or 10 per cent. When the enormous quantity of fuel for heating and the serious wear and tear of the retorts are considered, it becomes apparent that this process is much too costly. But the anthracene purified in this manner is the best material for preparing chemically pure anthracene; *cf.* p. 252 (Auerbach, *loc. cit.*).

It is sometimes asserted that pitch-anthracene suffers a considerable loss in this operation, but tar-anthracene none at all (?).

Perkin (*loc. cit.*) states that in this process no more anthracene is lost than in distilling without potash, but 40 or 50 per cent. of the impurities are removed. The phenols, he states, are retained in the residue, also a non-volatile compound of carbazol, of which sometimes as much as 10 or 12 per cent. occurs in crude anthracene; so that the distillate consists essentially of anthracene and phenanthrene. The alkaline process is indispensable for the manufacture of alizarin by means of dichloranthracene; and all crude anthracenes, even the worst, yield the same good quality. Anthracene, washed before distillation with naphtha and petroleum-spirit, yields again after distillation a considerable amount of impurities to those solvents (probably phenanthrene). [If the process possessed all these advantages not counterbalanced by any drawbacks, it is difficult to understand why it has been abandoned.]

In 1884 I saw at a large alizarin-works a process somewhat resembling that just described, viz., *fusing* (but not *distilling*) the anthracene, previously brought up to 50 per cent. by washing with caustic potash (not to be replaced by caustic soda); the carbazol is thus removed as a potassium salt, and the anthracene comes up to 60 per cent.

By washing the anthracene, distilled or fused, with caustic potash, solvent naphtha, etc., in the manner described, pp. 609 *et seq.*, the percentage of pure anthracene can be brought up to 70 per cent., or, as has been asserted, 80 or 90 per cent.; but the alizarin-makers do not seem to be inclined to pay the extra cost of such purification.

The Aktien-Gesellschaft für Anilinfabrikation in Berlin (Ger. P. 178764) fuses crude anthracene with caustic potash, and submits it to a distillation *in vacuo*, passing the distilling anthracene into solvents in which it is soluble at higher temperatures and allowing it to crystallize by cooling. Thus all commercial alizarines can be purified by a single operation; even where very much carbazol is present, 95 or 96 per cent. of the anthracene employed is obtained as an article of 95 to 98 per cent. real anthracene.

Rispler (*loc. cit.*) gives his results, obtained with the purification of anthracene by fusion with caustic potash. 'As stated *supra*, the process of refining low-grade anthracene by means of solvent naphtha causes a considerable loss of anthracene, owing to the presence of 14 to 18 per cent. carbazol, which is less soluble in that naphtha than the anthracene itself. Consequently before washing with solvent naphtha, the carbazol should be removed, which can be done because it combines with potassium hydroxide. Caustic potash is fused in an iron pan and kept at a temperature of about 230°; into this the tenfold quantity of crude anthracene is introduced, and the heating and stirring continued for about two and a half hours. When allowed to rest, the product of the reaction separates into two layers, the bottom layer consisting of potassium carbazolate, and the top layer of purified anthracene which is drawn off. In order to obtain a high yield, it must be avoided working with an excess of caustic potash which easily causes a decomposition of carbazol and alizarine; hence the crude alizarine should be previously tested for its contents of carbazol, and a quantity of caustic potash corresponding to this should be employed. By this process 100 kg. anthracene of 38·47 per cent., treated with 10 kg. caustic potash, yielded 73·2 anthracene of 47·86 per cent.. Hence 35·03 kg. pure anthracene have been recovered, with a loss of 8·94 per cent. From 50 kg. of this purified anthracene (of 47·86 per cent.), by washing with 75 kg. solvent naphtha, 29·7 kg. anthracene of 71·65 per cent. was obtained, with a loss of 11·07 per cent. By employing more solvent naphtha it is possible to get up to 80 per cent., with a corresponding loss of anthracene. If, instead of solid caustic potash, a 60 to 80 per cent. solution of potassium hydrate is employed, the loss by fusion is reduced from 8 to 3 or 4 per cent.

The *dehydration* of crude anthracene is effected by E. Wirth (Ger. P. 220214) by fusing it under pressure heating to 140° to 150°, whereby the water mechanically separates from the fused anthracene which is run out at the bottom; the small quantity of water still contained in it evaporates during the running out.

The preparation of *chemically pure anthracene*, as described by Znatowicz,[1] by nascent hydrogen in an acid solution, is hardly of technical interest (*cf.* also p. 252).

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[1] *Chem. Zeit.*, 1900, p. 772.

The men who are employed in the purification of anthracene are sometimes afflicted by a special *disease*, similar to the chlorine-ache.[1] As this disease only occurs through the direct contact of the skin with the crude anthracene, it can be kept off by great cleanliness, and by employing as much machine-work as possible.

Subliming the Anthracene.

Before anthracene, purified by any plan, can be converted into anthraquinone, it must undergo a suitable preparation (not merely by grinding) to reduce it to a sufficiently fine powder to facilitate the action of the oxidizing agents. For this purpose it is usually *sublimed* and precipitated in an extremely fine state of division by means of water. The sublimation is always effected by superheated steam, in an apparatus represented by Figs. 147 and 148[2] (or in a deeper still, fitted up in a similar manner). The anthracene is placed in a shallow pan, C, made of boiler-plate and heated from below, so that the anthracene fuses and forms a layer an inch or two in depth. The steam arriving in the pipe B is heated by the flame of the fireplace A to 220° to 240°, and issues from the flattened tube B′ (which is perforated by many holes) to the melted anthracene, which it causes to sublime and carries away through the wide delivery-tube F into the brickwork or wooden chamber D. In this a jet of water, finely divided by the rose H, descends, condenses the steam, and suddenly precipitates the anthracene brought over in the finest state of division. The partial vacuum caused in this operation no doubt assists the sublimation in C. After draining, the anthracene, now a white mass of fine scales, can, after passing it through a sieve to separate any coarser particles carried along in the melted state, be oxidized while still wet. The loss in this operation amounts to 2 or 3 per cent. According to Wurtz, the strength of the anthracene is thereby raised from 50 to 60-65 per cent.; but this is evidently a mistake. According to Auerbach (*loc. cit.*, p. 11), the effect of the sublimation is not a purification at all, but only a mechanical division. At any rate the purification cannot exceed the loss above mentioned of 2 or 3 per cent.; and this has been confirmed by all the alizarin-makers I have consulted. Sometimes no fire is applied to the still from without; but then the steam must be superheated to at least 300° and blown into the mass itself. The residue left in the still, when being cautiously distilled over a naked fire, yields carbazol, phenylnaphthyl carbazol, pyrene, and especially chrysene.

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[1] Russig, *Chemische Zeitschrift*, iv., p. 488 ; v., p. 315.

[2] From Wurtz, *Dictionnaire de Chemie*, Supplément, p. 65.

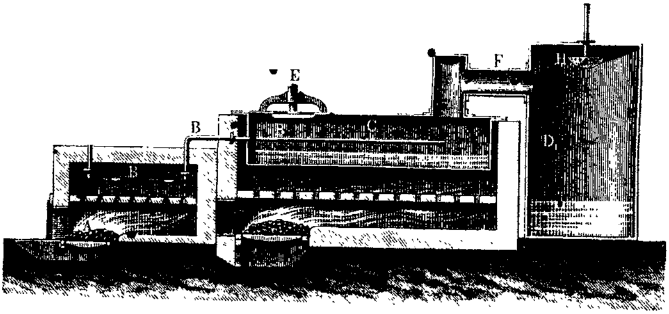


FIG. 147.

E. Perret (Wurtz, *loc. cit.*) proposes heating the anthracene to 250° and driving the vapour, mixed with air or carbon dioxide, by means of a fan-blast into chambers where it is

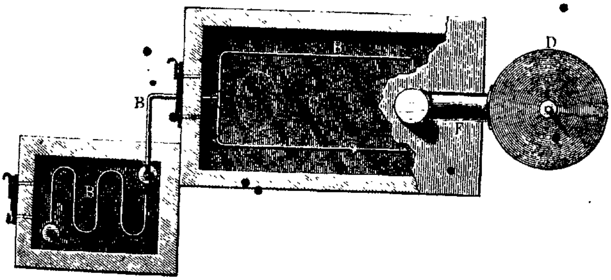


FIG. 148.

condensed in the dry way. A similar proposal was made by Schuller (*Berl. Ber.*, 1870, p. 548), but it does not seem so rational as the wet condensation.

Anthracene obtained synthetically.

Bradley and Jacobs (Ger. Ps. 125036 and 142051) obtain anthracene, together with benzene and naphthalene, by heating barium carbide with caustic baryta and soda to 600° to 1200° C. Thereby the hydrocarbons are obtained according to this equation (for benzene):

$$3BaC_2 + 3Ba(OH)_2 = C_6H_6 + 6BaO.$$

At present there is no chance of carrying out this reaction in a profitable way. Their patents were abandoned in 1904.

New Uses of Anthracene.

Up to now all the anthracene produced is consumed in the manufacture of colouring matters. Greening (U.S. P. 701713) proposes employing crude anthracene for the preparation of an electrically insulating and water-tight substance, by fusing it with barium carbonate for the removal of acids and impurities, drawing the fused mass off from the sediment, and fusing it, at a temperature not exceeding 215°, with copal, animé, or elemi resin; in order to obtain a plastic, flexible mass 1 part anthracene and 1 part of resin, and for obtaining a hard, non-flexible mass 1 part anthracene and 6 parts resin is to be fused together.

Preparation of Phenanthrene, Fluorene, and Carbazol, as By-products.

Very many endeavours have been made for utilizing these constant companions of anthracene, but up to the present without any practical results, partly because there was no sale for these substances, and partly because the expense of isolating was too high. Still, these attempts have not been thrown away, since they enable tar distillers to supply those compounds whenever they should be required by future inventors.

Especially *phenanthrene* appeared to have a chance of being applied in the synthesis of the opium alkaloids, as well as in that of colouring matters, and it might be obtained in large quantities from the washing-oils employed for purifying the anthracene, but this hope has not been fulfilled, and there is no interest manifested in the technical world for it.

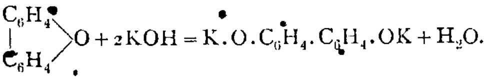
Phenanthrene can be obtained by fractional distillation of the above-mentioned anthracene residues, separating the portion distilling between 320° and 350°, and redistilling this portion, or recrystallizing the products. The first crystals consist of anthracene; the mother liquor drained therefrom yields phenanthrene which is obtained in the pure state by recrystallization. The anthracene might also be purified by its combination with picric acid (*cf. infra*, the methods of analysis).

The crude phenanthrene, as it is obtained in the form of anthracene residues, is an excellent material for the manufacture of *lampblack* (*vide supra*, pp. 373 and 610).

Kraemer and his co-operator, Weissgerber, have succeeded in preparing the hydrocarbons contained in the heavy tar-oils, boiling rather lower than anthracene, in the first instance phenanthrene and fluorene, by the action of fusing caustic potash on the respective tar-oils or by-products from the purification of anthracene. Patents for this have been taken out by the Aktien-Gesellschaft für Teer- und Erdöl-Industrie, Berlin (B. P. 5047, 1901; Ger. Ps. 111359, 124150, and 130679). Fluorene, similarly to carbazol (*cf.* p. 306), on being fused with caustic potash at 280° C., yields a solid potassium compound:

$$C_{13}H_{10} + KOH = C_{13}H_9K + H_2O.$$

According to the first German patent (124150), the fluorene is split off again from its potassium compound by treatment with water, after having previously removed the unattacked hydrocarbon floating on the potassic melt. This patent was not renewed after the first few years. According to the second patent (130679), the alkaline melt contains also diphenol-potassium, formed from the diphenylene oxide (p. 284):



$$\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!O + 2KOH = K.O.C_6H_4.C_6H_4.OK + H_2O.$$

It is not even necessary to remove the hydrocarbons floating on the top, but merely to treat the melt with water, which takes up the potassium compounds of diphenol and its homologues from which the latter can be recovered; the diphenol can be recovered by any acid, even CO_2. After the solid deposits from the high-boiling fractions of coal-tar have been well fractionated, the corresponding hydrocarbons may be immediately obtained in a pure form by means of this process; provided that these oils had been previously freed from acids and bases in the usual manner, and that the neutral liquid constituents had also been removed by combined pressure and heat.

Concerning the recovery of carbazol and phenanthrene from the pyridine solution in the process described on p. 615, we refer to that place.

Crude phenanthrene is used by Dreher (Ger. P. 118233; *Z. angew. Chem.*, 1901, p. 324) for preparing a rosin soap containing much free rosin for sizing paper. It is also used in the treatment of camphor, in lieu of naphthalene, for the manufacture of celluloid, as it does not possess the strong smell of naphthalene and does not evaporate so quickly.

Sulphonic acids of phenanthrene are used for making cresols soluble in water (Ger. P. 128880, Akt.-Ges. f. Teer- u. Erdöl-Industrie; B. P. 7119, 1901).

The literature on phenanthrene up to a few years ago is fully treated by M. A. Kunz in a special book: *Untersuchungen über Phenanthren* (Berlin, Julius Springer, 1902).

We lastly quote a number of recently published investigations on the companions of anthracene which hitherto possess only scientific interest, viz., the work of Thiele and his co-operators (*Ber.*, 1900, p. 851); Boes (*Pharm. Zeit.*, 1901, p. 915; *Chem. Zeit. Rep.*, 1901, pp. 315, 364); Moschner (*Ber.*, 1900, p. 757); Kraemer and Spilker (*Ber.*, 1900, p. 2263); Loeb (*Ber.*, 1901, p. 915); Bone and Jordan (*Chem. Zeit.*, 1901, p. 591); Dimroth (*Pharm. Zeit.*, 1901, p. 352), and many others in the following years.

Fluorene (see also p. 625) is prepared by the Gesellschaft für Teerverwertung Duisburg-Meiderich (Ger. P. 203312) by transforming the raw material into an alkaline compound which can be separated from the unchanged hydrocarbons. This compound is prepared by heating the material with sodium, or sodium amides, or sodium in the presence of ammonia, to temperatures between 110° and 250° C.; 300 parts of the mixture of hydrocarbons is heated during two hours with 20 parts of sodium, with agitation, to 150° to 200°. After cooling, the supernatant layer of unchanged hydrocarbons is mechanically separated from the fluorene compound remaining at the bottom. The latter is crushed and put into water, whereby fluorene is produced in the state of powder. It contains a small quantity of a high-boiling condensation-product, formed in the fusing process from the fluorene, from which it is separated by distillation *in vacuo*. When employing sodium amide, the reaction goes on at a lower temperature; it is sufficient to heat during an hour to 100° and another hour to 150° C. *Cf.* also Weger (*Z. angew. Chem.*, 1909, pp. 338 and 391).

Carbazol, the isolation of which from crude anthracene had been effected several decades ago by Graebe and Caro, had formerly no technical value whatever, and even now there is not much prospect of utilizing it. The Chemische Fabriks-Aktien-Gesellschaft in Hamburg (Ger. P. 81237) proposes to heat it in a pan gradually up to a bright red heat; carbon is separated and *cyanide of potassium* is formed, small proportions of carbazol, ammonia, etc, being removed by volatilization. The yield is increased by adding potash, soda, or similar substances during the fusion; and ferrocyanide can be obtained by the addition of iron.

We have already (*supra*, p. 625) mentioned the Ger. P. 111359 of the Aktien-Gesellschaft für Teer- und Erdöl-Industrie according to which carbazol is removed from crude anthracene and obtained as a compound with potassium.

Yields and Statistics.

The yield of anthracene varies both with the quality of the tar and with the care bestowed upon extracting it. While Scotch tar yields little or no anthracene, the German and Dutch works obtain from 0·3 to 0·35, at most 0·45, parts of pure anthracene (Luck's test) from 100 parts by weight of tar. In England the yield is much more considerable: North-Country tar, on the average, yields 0·5; London tar from 0·8 to 0·9 per cent. by weight of pure anthracene. From a communication by Mr J. Leahy, Thurston Chemical Works, Sittingbourne, it appears that the average yield of anthracene at that works for over eighteen months has been equal to 0·676 per cent. pure anthracene on the coal-tar distilled.

H. Elliott[1] states the yield of anthracene from water-gas tar as 2·63 per cent. [but that is hardly possible !].

Compare also the statements in Chapter V., pp. 504 *et seq.*

W. H. Perkin,[2] in 1885, estimated the yearly production of anthracene in the United Kingdom at about 6000 tons of 30 per cent., or nearly 2000 tons pure anthracene, which was largely in excess of the present requirements of the manufacture of alizarin. At that time the production of gas-tar in England was about 650,000 tons per annum; since then it has (inclusive of coke-oven tar) risen to upwards of 1,000,000 tons, and to this corresponds the production of pure anthracene which largely exceeds 3000 tons. This seems to make it a hopeless undertaking to manufacture anthracene by distilling pitch (*cf.* pp. 564 *et seq.*), or by superheating petroleum residues and the like (pp. 187 *et seq.*), or by distilling rosin with alkali, as patented by R. Irvine (B. P. 4276, 1882).

Anthracene is principally consumed in the German alizarin-works, which, according to reliable statistics, in 1880 worked up 1400 tons of *pure* anthracene, 200 tons of which were supplied by German tar-distillers, the remainder mostly by English distillers. Since then much more anthracene has been consumed, but the production has equally increased, in Germany mainly through the strong development of the coke-tar industry (pp. 161 *et seq.*). In consequence of this, the German anthracene market is no more altogether ruled by England, as it was the case in former times, but the English importation is still important. The German production of anthracene has for several years past exceeded that of England. According to official statistics, it amounted in 1908 to 4026 tons (pure), and is nowadays about 5000 tons (pure). In addition to this, the German alizarine makers have to import considerable quantities of anthracene from other countries, principally from England, but also from France, Belgium, and Austria-Hungary. This is proved by the following table of the importation of anthracene into Germany:—

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[1] *Amer. Chem. Journ.*, vi., p. 248 (1884).

[2] *J. Soc. Chem. Ind.*, 1885, p. 433.

Year.	Anthracene imported	Value.	Year.	Anthracene imported.	Value.
	Tons.	Thousands of Marks.		Tons.	Thousands of Marks.
1892 . .	5981	4785	1901 . .	3293	823
1893 . .	5523	4419	1902 . .	2876	590
1894 . .	3299	2639	1903 . .	2048	236
1895 . .	5913	5321	1904 . .	1230	172
1896 . .	6305	4729	1905 . .	1350	159
1897 . .	6490	3245	1906 . .	753	107
1898 . .	8027	3211	1907 . .	2418	257
1899 . .	4365	1746	1908 . .	2922	290
1900 . .	3894	1168	1909 . .	1650	167

The exportation of anthracene from Germany is quite insignificant. During four recent years it amounted to abou 400 tons (pure) for the whole time; all of this went t Switzerland.

Two qualities of anthracene are quoted in the market. *A* contains 40 to 45 per cent., *B* 25 to 40 per cent. pure anthracene According to *Chem. Trade Review*, 1887, p. 300, the former i obtained principally from Newcastle coals, and contains les paraffin and other troublesome impurities than *B* quality, whic is made from Lancashire and Yorkshire coal, with muc cannel-coal. The "unit" of trade means $\frac{1}{100}$ cwt. = 508 g *pure* anthracene.

The fluctuations in the price of anthracene are enormous Perkin (*loc. cit.*) paid per lb. in 1870-1871 1s. 6d., in 1872 1s. 6d to 5s. and even 5s. 6d. The value in 1881 was about 3s., in 188 about 9d.; in July 1887 it was 1s. 3d.; in August 1899 th London price for the unit of quality *A* (30 per cent.) was only 4d

In 1900 (*J. Amer. Chem. Soc.*, xxii., No. 9) Tayne state that the manufacture of anthracene (40 per cent.) from coal-ta had been abandoned for some years in the United States because its price was so low that it did not pay to make it as previously, for exportation to Europe.

Russig, in *Chem. Zeit.*, 1901, i., No. 2, shows the decline of prices of anthracene from 3½ marks per unit in 1890 to 0·4 mark in 1901 by a very instructive diagram.

According to *Bitumen*, 1910, No. 5, the price of anthracene in 1890 was 3 marks per 1 kg. (pure); in 1901 it had fallen to 0·35 mark, and in 1910 to 0·27 mark.

According to a communication from the German Syndicate of Tar Product Manufacturers, the price of anthracene in the English market has been nearly stationary since 1906, and amounts to 1½d. to 1¾d. per unit of the *A* quality. The German price has in the same years been equally stationary; it is 30 marks per 100 kg. pure anthracene for the ordinary 40 per cent. article, whilst that below 40 per cent., which is nowadays not called for, was 25 marks per 100 kg. pure.

Properties and Analysis of Anthracene.

The properties of *pure* anthracene have been described, pp. 250 *et seq.*

Crude anthracene, before sublimation, is a brownish-green friable mass, still containing most of the substances mentioned on pp. 589 *et seq.*

Zeidler[1] has made an extensive investigation of crude anthracene, and has found the following substances:—

I. Insoluble in acetic ether: anthracene, chrysene, and other bodies not yet examined.

II. Soluble in acetic ether.
  A. Soluble in cold 40 per cent. alcohol.
    1. Insoluble in carbon disulphide: carbazol.
    2. Soluble in carbon disulphide: phenanthrene, fluorene, hydrocarbons melting at 92°·5.
  B. Soluble in moderately warm benzene: synanthrene hydrocarbons melting at 97° and 104°.
  C. Soluble in hot benzene: anthracene, pseudophenanthrene.
  D. Insoluble in hot benzene: carbazol.

Methyl-anthracene is not mentioned by Zeidler, although it occurs largely in some descriptions of crude anthracene.

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[1] *Ann. Chem. Pharm.*, cxci., p. 285.

R. Kohn (Inaugural Dissertation, Munich, 1910) found in anthracene residues principally phenanthrene and carbazol with small quantities of diphenyl, fluorene, chrysene, biphenol and acridine.

It is not a very easy task to distinguish the different substances occurring in crude anthracene; and we cannot here go into this matter, which does not interest the tar-distiller so much as the alizarin-maker and the scientific chemist. We wil only mention that the identification of the different hydrocarbons is often promoted by the characteristic combinations they form with picric acid. Watson Smith[1] has proposed to employ the fused chlorides of antimony and bismuth for discriminating the solid hydrocarbons.

The details of these investigations are of greater interest for the manufacture of alizarin than for tar distillers. In this place we shall merely give the table drawn up by G. Schultz (*Chemie des Steinkohlenteers*, Braunschwerg, 1886, vol. i., p. 203), enumerating some of the properties of the most important substances present in crude anthracene.

	Formula.	Fusing-point.	Boiling-point.	Solubility in hot alcoho , benzene, etc.	Fusing-point of the picric acid compound.	Products of oxidation by chromic acid.
cenaphtene	$C_{12}H_{10}$	99°	280°	easy	123°	Naphthalic acid
luorene	$C_{13}H_{10}$	113°	295°	,	82°	Diphenyleneketone
henanthrene	$C_{14}H_{10}$	100°	340°	„	143°	Phenanthrenequinone and diphenic acid
arbazol	$C_{12}H_9N$	238°	355°	difficult	182°	...
nthracene	$C_{14}H_{10}$	213°	360°	„	170°	Anthraquinone, resisting CO_3
cridine	$C_{13}H_9N$	107°	above 360°	easy	...	...
luoranthene	$C_{15}H_{10}$	109°	„	„	183°	Diphenylene carbonic acid
seudophenanthrene	$C_{16}H_{12}$	115°	„	„	147°	A quinone, fusing at 17°
yrene	$C_{16}H_{10}$	149°	„	„	217°	Pyrenequinone
ethylanthracene	$C_{15}H_{12}$	200°	„	difficult	...	Anthraquinone carbonic acid and quinone
hrysene	$C_{18}H_{12}$	250°	„	„	163°	Chrysoquinone
arachrysene (Picene ?)	?	320°	„	..	..	...
henylnaphthylcarbazol (Chrysogene ?)	?	330°	„	„	.	$C_{16}H_8O_3$, $C_{16}H_9NO_2$, and phthalic acid

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[1] *Chem. News*, xl., p. 26.

The following table (by Becchi, *Berl. Ber.*, xii., p. 1976) describes the behaviour of these substances towards alcohol and toluene:—

	Formula.	100 parts Toluene dissolve		100 parts Absolute Alcohol dissolve	
		Cold.	At 100°.	Cold.	At boiling-point of the alcohol.
Naphthalene .	$C_{10}H_8$	At 16·5° = 31·94 parts	in all proportions	At 15° = 5·29 parts	in all proportions
Anthracene .	$C_{14}H_{10}$	16·5° = 0·92 „	12·94 parts	16° = 0·076 „	0·83 parts
Phenanthrene .	$C_{14}H_{10}$	16·5° = 33·02 „	in all proportions	16° = 2·62 „	10·08 „
Pyrene . .	$C_{16}H_{10}$	18° = 16·54 „	very soluble	16° = 1·37 „	3·08 „
Chrysene .	$C_{18}H_{12}$	18° = 0·24 „	5·39 parts	16° = 0·097 „	0·17 „

Considering the high price of anthracene, and the extremely varying percentage of pure anthracene in the rough product, it is evidently of the greatest importance to possess a reliable method of analysis. Formerly this was merely attempted by the action of solvents for the impurities, which, however, is so imperfect that those methods have been almost entirely replaced by Luck's method, which certainly requires some manipulative skill. But as the old methods are not yet altogether obsolete, we must here mention them.

Analysis of Anthracene.—*The solvent methods* were intended to remove the foreign matters and to leave pure anthracene behind. Evidently this cannot be done with any approach to exactness; for, on the one hand, the impurities are not entirely soluble (some are even less so than anthracene itself) in the liquids employed; on the other hand, the latter dissolve sensible quantities of anthracene as well. Hence different solvents yield quite discordant results; but, apart from the evident impossibility of thus ascertaining the true percentage of pure anthracene, each method by itself gives pretty constant results, on the condition of strictly keeping to the same mode of manipulation, which must be agreed upon between buyer and seller. The principal methods of this class were: the alcohol test, Perkin's petroleum spirit and carbon disulphide test, and Cohn's carbon disulphide test, with various modifications. They are fully described in our last edition, but we abstain from doing this now; since those methods have been proved untenable for commercial testing by the investigation of F. H. Davis and Lucas (*Chem. News*, xxix., p. 169; xxxi., p. 209) they have been entirely abandoned, both in England and in all other countries. The only method recognised as reliable for the valuation of anthracene is its transformation into anthraquinone, by the method worked out by E. Luck in the laboratory of the Forbwerke vorm. Meister, Lucius, & Brüning at Höchst-am-Main, which we shall describe below.

Obtaining an Average Sample.—To begin with, a proper *sampling* is very important. A 1½-in. hole is bored in both ends of each cask, and a 2-ft. steel tube, with wooden handle, cut open lengthways with sharp edges, is twisted into the cask from both ends right into the centre. The boring cores thus obtained are ground up and well mixed, and a reduced sample taken therefrom.

In quite the same way the sampling is performed if the anthracene is packed in bags.

Sampling tubes for this purpose have been described in detail by Gawalowski and by Angerstein, and these tubes are usually employed.

Anthraquinone Test.—Anthraquinone, the product of the oxidation of anthracene, obtained in the manufacture of alizarin, appears in the pure state as a mass of pale yellow needles, when precipitated from solutions, but in the shape of long, thin, golden-yellow needles when sublimed. It fuses at 277° and boils considerably above the boiling-point of mercury, but it sublimes very much below that. It is insoluble in dilute acids or alkalis, and is not even affected by hot concentrated hydrochloric acid or solutions of caustic alkalis; but it dissolves unchanged in concentrated sulphuric acid at 100°, and is again separated by dilution. It is very little soluble in alcohol and ether, but more so in hot benzene.

It had been previously recognised, especially by E. Kopp, that the oxidation of crude anthracene to anthraquinone, and the estimation of the latter, is the only reliable method of analysis in this case. But the merit of investigating all the points necessary to elaborate a system of testing belongs to E. Luck, whose name is justly attached to this test. Luck had first to ascertain whether a weighed quantity of rough anthracene, on oxidation with glacial acetic acid and chromic acid, yields the theoretic quantity of anthraquinone, whether the latter is not oxidized further by long contact with chromic acid, and what is the behaviour of the regular (accidental or purposely added) companions of anthracene during the chromic-acid treatment.

Höchst Test.—The method of testing the anthracene, founded by Luck on his investigation and practically used for some time, is described in our last edition. That description will not be repeated here, since it has been found that the method in its first shape was not quite accurate, and it has been entirely replaced by a modification, worked out at the factory of Meister, Lucius, & Brüning, at Höchst-am-Main, and known by the designation *Höchst test*, which is carried out as follows:[1]—Take 1 g. of anthracene, put it into a flask with condenser of 500 c.c. capacity, add to it 45 c.c. of glacial acetic acid, and heat to ebullition. To this solution, which is kept boiling, add drop by drop a solution of 15 g. of chromic acid in 10 c.c. of glacial acetic acid and 10 c.c. of water. The addition of the chromic-acid solution should occupy two hours, after which the liquid is kept boiling for two hours longer. The flask with its contents is to stand twelve hours, then to be mixed with 400 c.c. of cold water, and again kept standing for another three hours. The precipitated anthraquinone is now collected on a filter and washed, first with pure water, then with 200 c.c. of boiling dilute alkaline solution (1 KOH in 1000 water), and finally with pure hot water. The quinone is now washed from the filter into a dish and dried at 100° C.; it is then mixed in the same dish with 10 c.c. of fuming sulphuric acid of 68° Baumé (sp. gr. 1·88) and heated to 100° C. for ten minutes on a water bath. The acid should be pure and limpid and contain about 16 per cent. SO_3 in the free state. The quinone solution thus obtained is poured into a flat dish and kept for twelve hours in a damp place (say, on a thick layer of blotting paper, a glass jar being placed over it all) to absorb water; then add 200 c.c. of cold water to the contents of the dish, collect the precipitated quinone on a filter, and wash first with pure water, then with boiling alkaline solution, and finally with pure hot water. The anthraquinone is now placed in a platinum dish, dried at 100°, and weighed. After volatilizing the quinone by heating the dish, the latter is weighed with the residue of coal and the ashes. The difference between the two weights gives the weight of the anthraquinone obtained; and it is to be calculated in the usual manner into anthracene (multiplication by coefficient 0·8558). A correction for the quinone dissolved in the acetic acid is, under the conditions here prescribed, not necessary or admissible.

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[1] *Z. anal. Chem.*, xvi., p. 181.

The following table will save a calculation:—

Quinone	Anthracene.	Quinone.	Anthracene.	Quinone.	Anthracene.	Quinone.	Anthracene.
1	0·86	26	22·26	51	43·65	76	65·05
2	1·71	27	23·11	52	44·50	77	65·90
3	2·56	28	23·98	53	45·35	78	66·77
4	3·42	29	24·83	54	46·21	79	67·62
5	4·28	30	25·67	55	47·07	80	68·46
6	5·14	31	26·53	56	47·93	81	69·32
7	5·99	32	27·38	57	48·78	82	70·17
8	6·86	33	28·23	58	49·65	83	71·02
9	7·71	34	29·09	59	50·50	84	71·88
10	8·56	35	29·95	60	51·35	85	72·74
11	9·42	36	30·81	61	52·21	86	73·60
12	10·27	37	31·66	62	53·06	87	74·45
13	11·16	38	32·53	63	53·91	88	75·32
14	11·98	39	33·38	64	54·77	89	76·17
15	12·84	40	34·23	65	55·63	90	77·02
16	13·70	41	35·09	66	56·49	91	77·88
17	14·55	42	35·94	67	57·34	92	78·73
18	15·42	43	36·79	68	58·21	93	79·58
19	16·27	44	37·65	69	59·06	94	80·44
20	17·12	45	38·51	70	59·91	95	81·30
21	17·98	46	39·37	71	60·77	96	82·16
22	18·83	47	40·22	72	61·62	97	83·01
23	19·68	48	41·09	73	62·47	98	83·87
24	20·54	49	41·94	74	63·33	99	84·73
25	21·40	50	42·79	75	64·19	100	85·58

G. Schultz[1] holds that in one respect the Höchst test gives too unfavourable a result, since chromic acid converts methylanthracene into soluble anthraquinone-carbonic acid and thus removes it, whilst in the actual manufacture methylanthracene is converted into a quinone, and this into methylalizarin, which is said to have as much tinctorial power as alizarin. This, however, is not so; the products formed from methylanthracene impart to the alizarin colours a very objectionable shade, and hence alizarin-makers dread methylanthracene almost as much as paraffin (*cf.* Römer and Link, *Ber.*, 1883, p. 695). It occurs in large quantities only in the anthracene recovered from the washing-naphtha.

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[1] *Ber.*, 1877, p. 1051.

Holland[1] objects to Meister, Lucius, & Brüning's process (the "Höchst test"): 1st, that the 55 c.c. of glacial acetic acid, diluted though it be with 400 c.c. of water, still retains anthraquinone in solution, viz., on an average 0·0023 g.; 2nd, that boiling water dissolves some quinone, viz., 500 c.c. of water, 0·0019 quinone; 3rd, that in thrice washing the quinone from the filter a small loss is inevitable, which he estimates at 0·0020 g.; even with the most careful manipulation the total loss amounts to 0·0065 quinone = 0·0055 anthracene, and this quantity should always be added to that found. (According to information received by me from a most reliable authority, Holland's corrections are inadmissible, as the anthraquinone obtained by the Höchst test is itself not quite pure, but contains methylanthraquinone, anthraquinone-carbonic acid, and paraffin, which may cause an error of 1 per cent. and upwards in the opposite direction to Holland's corrections.)

Anthraquinone, as obtained by the Hochst test, ought to be crystallized and of pale yellow colour. An orange or red colour indicates the presence of other quinones, especially those of phenanthrene and chrysene. The latter is also recognized by the production of an indigo-blue coloration on adding the sulphuric acid. In the case of impure anthraquinone, both the acid filtrate and the alkaline washings are deeply coloured. The above-mentioned quinones do not prevent the crystallization of anthraquinone, but this is done by the quinone, $C_{16}H_9NO_2$, produced by the oxidation of the imido-phenylnaphthyl (see below), which is one of the sources of the so-called "amorphous particles." This impurity can be destroyed by a somewhat longer-continued heating with sulphuric acid, which ought hence never to be omitted when crude anthraquinones of suspicious appearance have been obtained (Allen, *Commercial Organic Analysis*, 2nd ed., ii., p. 532).

Basset (*Chem. News*, lxxiii., p. 73) proposes boiling the quinone, obtained according to Luck's method, for some time with a mixed solution of chromic and nitric acid; pure anthraquinone does not lose weight, but that obtained from commercial anthracene loses 1 or 2 per cent. or more. Later on (*ibid.*, lxxix., p. 157) he pointed out the fact that acetic acid sometimes reacts on chromic acid, which might be a source of error. Pure glacial acetic acid (16°·7 fusing-point) reduces in the cold 0·16 g. chromic acid (out of 15 g.) in twenty-four days, and 4·44 g. on boiling four hours under the same conditions as in Luck's test; less pure glacial acetic acid (13°·3 fusing-point) reduces under the same conditions 0·87 g. chromic acid in the cold, or 6·45 g. on boiling. These lower grades of acetic acid cause "high" results, by reducing the strength of the chromic-acid solution on keeping.

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[1] Printed circular, dated Manchester, February 1879.

A. G. Perkin (*J. Soc. Dyers and Col.*, April 1897) points out that nothing certain is known as to the nature of the impurities destroyed by the action of fuming oil of vitriol on anthraquinone. They are probably chromium compounds of the carbon-acids or phenols formed during the oxidation, and decomposed only by heating with oil of vitriol. The quality B of crude anthracene, which requires special processes to yield good alizarin, is recognized by the presence of felt-like masses, the nature of which is not clearly known; it frequently contains β-methylanthracene, and in doubtful cases should be tested by converting it into alizarin.

Mr B. Nickels has communicated to Mr Allen (*loc. cit.*) the following process for testing anthracene, employed at some alizarin-works, of which the aim is to work as closely as possible according to the method of oxidation pursued on a manufacturing scale. With this view, the oxidation is carried out in very dilute liquids, under which conditions the anthracene is converted into anthraquinone, while the foreign hydrocarbons suffer but little change. On subsequently treating the product with sulphuric acid, the unoxidized hydrocarbons are converted into soluble substances, and nearly pure anthraquinone results, which may be obtained perfectly pure by a second treatment with acid. In experienced hands and with careful manipulation, this miniature factory-operation gives constant and very accurate results. The chief source of error is the incomplete conversion of the anthracene itself, and its consequent solution and loss on treating the crude anthraquinone with sulphuric acid; but this can be guarded against by a microscopic examination of the oxidation-product. The following are the details of the process:—Ten grammes of the sample of anthracene are ground to an impalpable powder in a mortar; 20 g. of potassium bichromate are added, and the whole is thoroughly mixed by grinding. The mixture is transferred to a large porcelain dish, 1 litre of water added, and the liquid made to boil. Thirty g. of sulphuric acid are diluted with about an equal measure of water, and added in successive small portions during about one hour, the liquid being kept constantly boiling and frequently stirred. The boiling is continued for three hours after the whole of the acid has been added, care being taken to replace the loss by evaporation by adding boiling water, as it is only in a dilute solution that the anthracene can be converted into anthraquinone, without simultaneously oxidizing the accompanying substances. The liquid is next filtered, and the filter washed with hot water till all traces of chromium-salts have been removed. The contents of the filter are then dried at 100° and weighed. The weight obtained represents the yield of "crude factory anthraquinone," and may contain from 40 to 50 per cent. of the pure substance. Before purifying this crude product, a minute quantity of it should be dissolved in hot benzene and a drop of the solution placed on a glass slide. After allowing the dissolved matters to crystallize, a glass cover is applied, and the slide observed under the microscope. Unoxidized anthracene, if present, assumes the form of sharp, tabular, overlaying plates; while the anthraquinone will be in the form of distinct needles and stellated groups. Naphthalene is the only associated hydrocarbon which at all simulates anthracene, but with a little care it is readily distinguished. The other bodies likely to be present assume more or less characteristic forms, which cannot be confounded with anthracene. Examined with the polariscope, the appearances of anthracene and anthraquinone are extremely characteristic. If no unoxidized anthracene be detected under the microscope, the purification of the crude anthraquinone is proceeded with as follows:—

The crude anthraquinone is next treated in a small shallow dish with four times its weight of strong sulphuric acid; and the mixture is heated in the water-oven for about an hour and a half, being frequently stirred during that time. The capsule is then placed in a box, or under a bell-jar, side by side with a larger dish of boiling water, so as to maintain a moist atmosphere, which causes the gradual dilution of the acid and facilitates the crystallization of the anthraquinone. After twelve hours the capsule is removed and immersed in about 500 c.c. of water, which is then boiled. After cooling, the liquid is filtered, the residue washed till free from acid, and then treated on the filter with a dilute boiling solution of caustic soda (sp. gr. 1·04), till the filtrate runs through colourless. The alkali is then washed out with warm water, and the substance on the filter dried at 100° C. and weighed. The product has a greenish-grey or slate-grey colour, is highly crystalline, and contains from 80 to 95 per cent. of real anthraquinone. A known weight of it (about 1 g.) is further purified by heating it in the water-oven for ten minutes with ten times its weight of strong sulphuric acid. The product is exposed to a moist atmosphere, dissolved in water, filtered, treated with alkali, etc., and weighed in a manner exactly similar to that previously adopted. The usual precautions respecting the treatment of the anthraquinone on the filter should be observed here. The weight of pure anthraquinone obtained is calculated first on the grey product, and then on the original sample, or intermediately on the crude anthraquinone, if some of the latter was not recovered from the benzene solution used for its microscopic examination. The pure anthraquinone found, multiplied by ·856, gives the real anthracene in the sample.

It should be stated that the anthraquinone test, even in its most perfected form, does not give absolutely reliable results. Sometimes a certain description of quinone, which is as beautifully crystallized as possible, and cannot be distinguished by any outward marks, yields very inferior alizarin. The cause of this is as yet unknown; but it is most likely that the quinone in such cases contains not merely pure anthraquinone, but also the derivatives of hydrocarbons other than anthracene, which are so similar to anthraquinone in appearance and chemical properties, that at present no means are known of separating them from anthraquinone itself. Some authorities have asserted that these inferior quinones are more easily soluble in glacial acetic acid; but no proof of this has been given, and we must hold this question as not yet solved.

We mention also a plan for *estimating the quantity of anthracene present in tar*, although it does not appear to be very correct, the quantity of tar worked upon being so very small. C. Nicol (*Z. anal. Chem.*, 1876, p. 318) distils 20 g. of tar, and collects the vapours in a U-tube kept at 200° C. by means of a paraffin-bath. Here the more volatile oils go away, whilst anthracene, etc., remain behind. Since a little remains in the neck of the retort, this is cut off, the glass is pounded and added to the distillate in the receiver. This is now dissolved in glacial acetic acid, and the anthracene estimated by Luck's test. (In testing tar, I distil at least 1 litre at a time, and estimate the anthracene in the oil coming over between 270° and the end of the distillation.)

Detection and Estimation of the Impurities contained in Commercial Anthracene.

Imido-phenylnaphthyl, which impedes the purification of the anthraquinone, can, according to B. Nickels (*Chem. News*, xl., p. 270; xli., pp. 52, 95, 117) be discovered by dissolving the sample of crude anthracene in hot benzene, filtering through a dry filter, and examining the solution with a spectroscope. The above substance produces a highly characteristic absorption-spectrum, showing two broad and well-defined black bands between the F and G lines, and another slightly more refrangible than G.

Methylanthracene.—This very unwelcome substance occurs principally in anthracene prepared from gas-tar, obtained in cases where cannel-coal had been used for gas-making. If it is present, the anthraquinone obtained in the analysis of the anthracene does not appear in the usual needle-shape, but as a felted mass. Schultz and Papp (*Berl. Ber.*, 1877, p. 1049), who were the first to discover methylanthracene in crude anthracene, describe a method for separating it, viz., oxidizing the anthracene by potassium bichromate and sulphuric acid, distilling the residue, and treating the distillate with alcohol; from the alcoholic solution the phenanthrene crystallizes out, and from the mother liquor the methylanthracene can be prepared. A. G. Perkin (*J. Soc. Dyers and Col.*, April 1897; *Chem. Centr.*, 1897, p. 447) declares that the best valuation of anthracene containing methylanthracene takes place by working it up for alizarine.

Paraffin, the objectionable presence of which in some samples of anthracene has been mentioned on p. 614, can be detected and determined in the following manner:—Ten grammes of the sample is heated with 200 g. of strong sulphuric acid in a water-bath for about ten minutes, or until the anthracene is completely dissolved. Any considerable quantity of paraffin will rise to the surface in the form of oily globules. The solution obtained is cautiously poured into 500 c.c. of water contained in a tall beaker. After being thoroughly stirred, the liquid is allowed to cool, when any paraffin will rise to the surface, and having solidified, can be removed, washed with a little cold water, dried between blotting-paper and weighed. From 2 to 5 per cent. is the quantity usually present in Scotch anthracenes (Allen, *Commercial Organic Analysis*, 2nd ed., ii., p. 529).

Heusler and Herde[1] estimate the paraffin by placing at least 2 g. of crude anthracene into a flask holding 150 c.c., and adding, at first drop by drop, and cooling with ice-water, 25 c.c. fuming nitric acid. When all the acid has been added, the whole is digested until the anthracene is dissolved, then heated on the water-bath till all the paraffin is melted. The latter after cooling is collected on a small filter and mixed with fuming nitric acid, until the filtrate does not become opaque on the addition of water. Then the washing is continued with water, until the acid reaction has ceased. Now a test-tube is placed under the filter and the paraffin is washed into this, first with alcohol, then with warm ether. The alcoholic solution is evaporated in a small porcelain dish on the water-bath; afterwards the ethereal solution is added and is also evaporated; the paraffin is dried for half an hour at 105° or 110°, and weighed.

Kraemer and Spilker (in *Muspratt-Bunte*, viii., 70) recommend the following method as very accurate:—Shake 10 g. of the very finely-ground anthracene in a 100 c.c. flask with 70 c.c. ether for ten minutes, fill with ether up to the 100 c.c. mark, mix, and put aside for settling. Put 50 c.c. of the clear solution into a porcelain dish, allow the ether to evaporate, and dry the residue at 100° for half an hour. After cooling, triturate it finely, add 8 c.c. fuming sulphuric acid (with 20 per cent.

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[1] *Z. angew. Chem.*, 1895, p. 253.

anhydride), mix well, cover the dish with a watch-glass, and heat for three hours at 100° C., frequently stirring. Wash the contents of the dish, by means of 500 c.c. hot water, into a beaker, and after cooling, pass through a dry filter and wash this and the beaker with cold water until barium chloride does not produce a cloud in the filtrate. Allow the filter to drain thoroughly, moisten it with absolute alcohol, and wash the paraffin by means of ether into a weighed dish until a few drops of the running-off ether do not leave any residue on evaporation. Remove also the last traces of paraffin from the beaker by means of ether. Evaporate the ethereal solution in a moderately hot place, dry the residue at 105° C. for half an hour, and weigh it as pure paraffin.

The following process for estimating small quantities of paraffin in anthracene is recommended in *The Oil and Colourman's Journal*, 1906, p. 487 (*Z. angew. Chem.*, 1907, p. 463). Heat 10 g. of the anthracene with 108 g. concentrated sulphuric acid in a beaker on the water-bath till dissolved, and after cooling pour into 400 c.c. cold water. Extract the solution by shaking it twice with petroleum spirit; mix the extract first with half its volume of 5 per cent. caustic soda solution, then four times with one-eighth of its volume of cold concentrated sulphuric acid, and lastly, remove the acid by washing with water. Now distil the residue from a tared flask; the residue, multiplied by 10, indicates the percentage of paraffin.

Analytical Methods for Carbazol and Phenanthrene.[1]—Carbazol can be estimated in two ways. Either remove the basic compounds by means of warm, dilute sulphuric acid, estimate in the residue the nitrogen by Kjeldahl's method, and from this calculate the carbazol. Or else proceed in the following manner:—

In a very thick-walled steel crucible, Fig. 149, holding 80 c.c., in whose very thick sides there is a hole drilled for a thermometer, 40 g. caustic potash of 80 to 85 per cent. KOH are melted. Keep the temperature at 180° to 200° C., and with constant stirring introduce 20 g. of crude carbazol (or crude anthracene). Take away the top part, put any matter sublimed into it back into the crucible and volatilize the anthracene and other concomitant substances at a temperature *not exceeding*

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[1] From *Muspratt-Bunte*, viii., 71.

270° C. For this two hours suffice in the case of high per cent. carbazol. Longer heating should be avoided. Triturate the cold melt with hot water and add dilute sulphuric acid until the acid reaction is distinct. Put the carbazol thus set free on to a filter, wash and dry. The product is usually of a dark colour and must be purified with toluene, of which for high per cent. carbazol 600 to 800 c.c. are required. Pour the boiling toluene solution through a plaited filter and wash the flask and the filter with a small (measured) quantity of boiling toluene. From the (usually brown) solution part of the carbazol crystallizes out; this, after twelve hours' standing at 14° to 18° C., is drained by aspiration on a filter disk and weighed. The filtrate is measured at 17° C., and for each 100 c.c. 0·48 g. carbazol is allowed as contained in the solution. In the end 0·5 g. carbazol must be added as a correction of the quantity found.

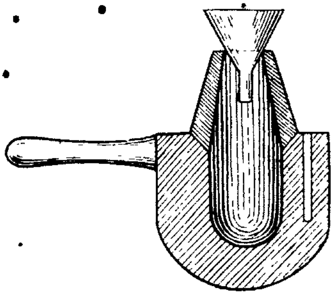
FIG. 149.

Vautel (*Z. angew. Chem.*, 1891, p. 748) estimates carbazol by titration of its solution in glacial acetic acid by means of potassium-bromate solution with addition of potassium bromide up to a permanent reaction for bromine. For 2 mol. bromine only 1 mol. carbazol is used up.

Estimation of Phenanthrene.—This is more difficult than that of anthracene and carbazol. The following method (communicated by Kraemer and Spilker) gives tolerably reliable results only in the case of a material rich in phenanthrene. For estimating it in crude anthracene the percentage of phenanthrene is increased as follows:—Dissolve 1 kg. crude anthracene in 2 kg. toluene and allow to crystallize at the ordinary temperature, with frequent stirring for six hours. Separate the liquor after drawing it off by a vacuum pump and washing with 200 c.c. toluene from the anthracene and carbazol, which had been separated as crystals, and remove the toluene by evaporation. The residue thus obtained is submitted to fractional distillation, and the product passing over between 280° and 340° C. is considered as rough phenanthrene and treated as follows:—20 g. of it is heated with a solution of 30 g. picric acid in 300 c.c. dry xylene in a flask with reflux cooler. The crystals separated after standing for twenty-four hours, during which time the mass should be strongly shaken up several times, are collected on the vacuum pump, dried, and weighed as crude picrate. The mother liquor is diluted with 50 c.c. xylene, and in it once more 20 g. crude phenanthrene and 30 g. picric acid are dissolved. The difference between the quantity of rough picrate now obtained against the weight of the first crop of crystals shows the rough picrate dissolved in 250 c.c. xylene. From the solubility factor thus obtained and the weights of the crops of crystals we find the total weight of the rough picrate formed from 40 g. of the crude phenanthrene. A weighed portion of this is recrystallized from 95 per cent. alcohol. To the weight of the pure picrate, separating in the shape of shining yellow-red needles, that dissolved in the alcohol (20 g. for 750 c.c. 95 per cent. alcohol) must be added. It is better to convince one's self of the purity of the last-obtained picrate, by decomposing it with ammonia, washing the hydrocarbon with dilute sulphuric acid (to remove any acridine, possibly present), and weighing the remainder; 100 picrate = 43·7 phenanthrene. In the case of very impure phenanthrene it is preferable to work upon 30 g. each time, allowing 45 g. picric acid and 200 c.c. xylene (in lieu of 50 c.c.) after the first crystallization. The difference of both crystallizations now represents the solubility of rough picrate in 100 c.c. xylene.

The following *qualitative reactions* for the *discovery of carbazol and phenanthrene* are given by Behrens.[1] For carbazol extract with acetic ether in the cold, allow the liquid to evaporate, and put the residue on to a watch-glass, with a few drops of acetic ether; the carbazol, remaining behind on evaporation on the margin, when being moistened with a drop of nitrobenzene and phenanthrene quinone, yields characteristic copper-coloured scales. For phenanthrene, extract with benzol and test with a solution of dinitrophenanthrene quinone in nitrobenzene (*cf.* also, *Chem. Centr.*, 1901, i, 796).

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[1] *Chem. Centr.*, 1902, ii., 540.

Examination of the Commercial Products obtained from filtered Anthracene Oil.

Carbolineum.—On pp. 605 *et seq.* we have given a general description of the products sold by that designation. Their examination would comprise the determination of specific gravity by the usual methods; of the deposits of solid substances at the ordinary temperature; a fractional distillation in the way described *infra*, by which at the same time any water present would be found; the nature of the residue from the distillation (whether crystalline or pitchy); the determination of the viscosity by Engler's method; of the inflaming-point according to Pensky's method; and the composition of the ashes. Frequently it may be important to prove any adulteration by hydrocarbons of the aliphatic series, particularly water-gas tar, which can be easily performed by shaking up with dimethyl sulphate, according to the method of Valenta and Graefe, which will be described in the next chapter.

Nördlinger (*Pharm. Zeit.*, 1907, p. 1097) examines carbolineum and similar products by soaking them up in blotting-paper, determining the loss of weight by the volatilization of the lighter oils, and extracting the residue by ether. Good oils ought to show but a slight loss of weight, and after the evaporation of the ether they ought to retain the oily properties.

Absorbing-oil.—The oil prepared by the method of Bueb (p. 607) for the purpose of washing the naphthalene out of coal-gas (which is performed in order to prevent an obstruction of the gas-pipes by naphthalene), which is obtained by repeatedly distilling the anthracene oil, and removing the fractions boiling below 270°, and which is sent into the trade either in that state, or after adding 4 per cent. of benzol, is examined as follows:—One hundred c.c. of the oil are distilled in a bulb of 300 c.c. capacity, provided with a two-bulb tube at the top, a thermometer, and a cooling-jacket 300 mm. long, at a rate of one drop per second from the cooler, making two fractions (1) at 200°, (2) at 270°. The oil containing an addition of 4 per cent. benzol ought to yield, apart from the benzol coming over up to 120°, at most 2 per cent. (by volume) up to 200°, and from 4 to at most 8 per cent. between 200° and 270°. The less distils between 200° and 270° the better is the quality of the oil. When distilling oil containing no benzol, the first fraction ought to be less by 4 per cent. Both fractions, when cooled down to 0° for an hour, ought not to separate any naphthalene.

On the estimation of the absorbing quality of such oils, we refer to the prescriptions of Hodurek, p. 605, Ellery, p. 608, and Bayer, p. 608.

CHAPTER VI

PITCH

IT need hardly be said that the word "pitch" denotes many substances which have nothing to do with coal-tar, such as pitch from petroleum, wood, natural bitumen, and some products obtained in the manufacture of stearine, wool, etc. Donath and Margosches (*Chem. Ind.*, 1904, p. 221) discourse on these various descriptions of pitch and asphalt and their distinctions from coal-tar pitch. In this book we treat exclusively of the latter.

The nature of coal-tar pitch is very little elucidated up to the present. We shall presently quote statements on the ultimate analysis of pitch, and on the amount extracted by various solvents, but this evidently does not lead to a knowledge of the chemical compounds constituting the pitch. Aug. Lemoine, in a pamphlet published in 1902 under the title *Sur la connaissance des brais minéraux* (Charleroi), contends that coal-tar pitch is a mixture of carbon, of "carbures," and "carbenes." About the so-called "free carbon" we shall presently say more; all are agreed that it contributes nothing to the plastic and agglutinating properties of the pitch. The "carbures" are at the ordinary temperature a brownish green or black mass, like butter entirely fluid at 45° to 50° C.; they impart to the pitch its plasticity and its power to glue together pulverulent substances into solid masses. The designation of "carbenes" has been given by Lemoine to a black, crystalline, shining powder which he found in pitch, softening and fusing about 200° C. At that temperature it swells up and spreads on the glass, adhering to it but slightly. The chemical nature of these compounds varies very much, but anyhow they are non-saturated compounds, as they combine with bromine. They impart to the pitch the property of being solid at ordinary temperatures; they contribute but little to its agglomerating properties, but they are indispensable, because without their presence the tar would be too glutinous; the briquettes, etc., would adhere to the moulds, and would be too soft and easily deformated; but if there is too much of them present, the briquettes would be too little compact. Lemoine gives some tables on the percentage of agglutinating substances in various pitches, and on their degree of plasticity, but as he does not indicate how his results are obtained, we abstain from going into his figures. We refer here also to the investigations of Carnelly on the soluble constituents of coal-tar pitch (*supra*, p. 264).

According to Kraemer, it may be assumed that coal-tar pitch generally contains about 60 per cent. of soluble "asphalt," of the formula $C_{2n}H_n$, and about 40 per cent. of substances of the formula $C_{8n}H_n$, as well as free carbon and other insoluble substances. Of course pitch also contains some of the highest-boiling constituents of coal-tar, as anthracene, phenanthrene, chrysene, pyrene, carbazol, etc.

Kraemer (*Chem. Ind.*, 1903, p. 303) develops his ideas on the formation of coal-tar pitch. Certain non-saturated compounds—*e.g.* indene—are polymerised and subsequently decompose by heating, the hydrogen changing its position within the molecule. On one side one molecule of hydrindene, containing 2H more than indene, is formed, on the other side truxene, which contains 6H more than indene and has a high melting-point:

$$4C_9H_8 = 2C_9H_{10} + C_{18}H_{12}.$$

Similar additions with subsequent splitting-up appear to occur with many other non-saturated components of the products of tar distillation, possibly also with compounds containing O and S, and it may be assumed that the pitch consists essentially of substances formed in this manner, of very high boiling-point.

Elementary Composition of Coal-tar Pitch.

Constam and Rougeot (*Glückauf*, 1906, pp. 406 *et seq.*)

found the following percentages of elementary substances in soft and middling hard pitch:—

	Soft pitch.	Middling hard pitch (Patent-fuel pitch).
C	61·60 per cent.	85·14 to 92·59 per cent.
H	4·89 "	4·85 to 4·60 "
O + N + S	3·20 "	7·87 to 2·77 "
Ashes	0·31 "	2·54 to 0·04 "

C. R. Downs (*J. Ind. Eng. Chem.*, 1914, vi., p. 206) found the composition of three typical American brands of pitch for the manufacture of patent fuel:—

	Per cent. No. I.	Per cent. No. II	Per cent. No. III.
C	92·05	92·37	93·09
H	4·83	4·96	5·01
N	0·95	0·61	0·89
S	0·92	1·00	0·85
Ashes	0·09	0·78	0·35
O	1·16	0·28	0·00
C (free)	35·7	31·3	26·4
Fusing point	112°	87°	84°

Something on the essence of coal-tar pitch can be learned from the products of its destructive distillation, to be described later on. In this process, besides solid and liquid hydrocarbons of the naphthalene and anthracene series, there are formed benzene, aqueous vapour, and ammonia, together with other gaseous substances. According to Watson Smith (*J. Soc. Chem. Ind.*, 1892, p. 119) the smell of ammonia is only perceived after the coking (during the cooling of the coke in the air), and Alder Wright in this case also observed the smell of cyanogen. Staveley (*Chem. News*, xliii., p. 228) found in pitch coke only 0·11 to 0·12 per cent. sulphur, a proof of the fact that most of the sulphur contained in pitch during the coking process goes into the volatile compounds.

In the ordinary *solvents* pitch is more or less soluble, not to a great extent in ethyl- or methyl alcohol, more easily in ether and petroleum spirit, very much so in chloroform, carbon disulphide, and benzol, most easily and completely in the phenols, aniline and pyridine bases. These solutions, which are coloured brown up to black, are characterized by a blue-green fluorescence, differently shaded according to the solvent, when lighted from the outside.

General Properties: Hard and Soft Pitch.

We have seen in the preceding chapter that the distillation of coal-tar leaves a more or less consistent residue, according to the way in which it has been conducted. If only the light oil is distilled off (that is, if the process is stopped when the specific gravity of the distillate equals that of water), the residue in the retort (about 80 per cent. of the weight of the tar) is sometimes called *asphalt* (*brai liquide*). It is very unusual now to carry on the process in this way; what is called "asphalt" by tar-distillers is made by mixing ordinary pitch with a suitable quantity of creosote oil, and most commonly it is soft pitch mixed with sand, etc. (*vide infra*).

If about 10 per cent. more is distilled off, the residue is *soft pitch*; next comes moderately hard pitch; and *hard pitch* is obtained if the process is carried on as far as wrought-iron vessels will permit (p. 468). Another rule is this: *Soft pitch* is obtained if the distillation is interrupted before driving off the anthracene, when the specific gravity of the distilling oils is about 1·090; *hard pitch*, if it is continued till the oils show sp. gr. 1·120; moderately hard pitch, if the distillation is interrupted between these two stages.[1] These indications certainly vary according to the quality of the tar, its contents of free carbon, etc.

The specific gravity of pitch depends upon its degree of hardness, and even more upon the material from which the tar has been obtained. It is = 1·25 to 1·275 in the case of pitch from vertical stills and from coke-oven tar; pitch from gas-tars, rich in free carbon, shows a specific gravity not below 1·30 to 1·44, whilst pitch from water-gas tar and oil-gas tar rarely exceeds 1·20 sp. gr.

Soft pitch softens at 40° and fuses at 50°; at ordinary temperatures it is soft, and only at lower temperatures it can be broken into pieces which re-unite after lying for some time.

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[1] The manufacture of pitch from coal-tar without distillation, by a treatment with sulphuric acid, has been mentioned, *supra*, p. 366.

It is very shiny on the fraction surfaces; when lying in sunshine, it soon runs together into a viscous mass, showing a mirror-like lustre.

Middling hard pitch (briquette pitch) softens at 60° and fuses at about 70°. At ordinary temperatures it is hard and easily broken into pieces, which, however, have no sharp edges. When exposed to sunshine, it soon collapses into a shapeless mass.

Hard pitch softens at 80° to 85° and fuses between 90° and 100°. On being broken up it yields sharp-edged, sounding pieces of slight lustre, which resist the action of sunshine very well.

The *asphalt*, if obtained by merely distilling off the light oils, naturally contains all the constituents of creosote oil (that is, naphthalene, phenols, etc.), together with all higher-boiling substances. Proper "pitch" always contains the least volatile components of coal-tar, such as anthracene, phenanthrene, chrysene, pyrene, etc., together with several ill-defined substances, as bitumen, etc., and free carbon, or rather coal-dust or coke-dust in an extremely fine state of division. It is, however, possible that something nearly approaching real carbon, or graphite, formed by the decomposition of tar-oils on the hot sides of the retorts, is also present in coal-tar. The value of coal-tar is greatly diminished if there is a considerable quantity of such "free carbon" present, which always comprises coal-dust or coke-dust as well (*cf. supra*, pp. 394 and 523, and *infra*).

Behrens,[1] by successively digesting hard pitch, freed from all oils up to sp. gr. 1·120, with cold benzene, carbon disulphide, boiling benzene, and boiling alcohol, obtained 23·54 per cent. of a black powder, containing 90·856 C, 3·058 H, and 0·398 ashes; when treated somewhat differently, the residue yielded 91·921 C, 3·157 H, and 0·872 ashes, quite similar to South Welsh anthracite (*cf.* the patent of E. Heusser, further on).

According to Habets,[2] good hard pitch consists of 75·32 per cent. C, 8·19 H, 16·06 O, 0·43 ash, and its sp. gr. is 1·275 to 1·286.

Donath and Asriel,[3] in examining soft pitch, moderately hard pitch, and hard pitch from the same factory, obtained with it the following results per cent.:—

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[1] *Dingl. polyt. J.*, ccviii., p. 369.

[2] Gurlt, *Steinkohlenbriquettes*, p. 23.

[3] *Chem. Centr.*, 1903, i., p. 1099.

	C	H	N	S	Extract with petroleum spirit.	Extract with benzene.	Extract with CS_2.	Residue.
Soft pitch . .	91·8	4·62	?	?	25·05	44·98	6·57	22·82
Intermediate pitch	94·32	3·98	0·148	0·77	15·14	40·03	7·10	38·16
Hard pitch . .	93·16	4·36	?	?	15·51	39·46	15·71	29·39

Hard pitch, on being extracted with petroleum spirit of 56° to 60° boiling-point, yielded a very tough, viscous residue, containing 2·19 per cent. anthracene. The extractions with benzene and that with CS_2 followed in rotation. The last residue was a non-lustrous, deep black powder, containing 89·2 C, 2·3 H, 0·7 N, 7·13 O, 0·67 ashes (O calculated from difference). The constituent which imparts the black colour to pitch is comparatively the richest in oxygen. Part of this residue is undoubtedly more or less unchanged coal-dust.

Hard pitch is easily divided into flakes or lumps, which do not soften even in the sun, and can be always sent out in bulk, whether in railway-trucks or in ships, at all seasons of the year. Moderately hard pitch can be sent out in bulk in railway-trucks, but not in ships, where it would coalesce into a mass, at least in the warm season. Hence the English tar-distillers mostly make moderately hard pitch; and so do the French, at least in summer. Soft pitch can only be sent out in casks, and is mostly run into these direct from the tar-stills. According to the Alkali Inspector's Report for 1893, p. 114, 95 per cent. of the pitch made in England is sold in the medium-hard stage, after distilling up to hard pitch and softening it with creosote oil; only 1 or 2 per cent. is sold in the state of hard pitch, and 3 or 4 per cent. as soft pitch.

The manufacturers of patent fuel, especially in Belgium, greatly prefer soft pitch to hard; hence the German tar-distillers are compelled to make at most only moderately hard pitch. During the winter months much soft pitch is sent out to those works which require in summer a moderately hard or even decidedly hard pitch.

Where it is not possible to soften the pitch while it remains liquid in the still, or else in the pitch-cooler, by pumping in oils, the operation is more complicated. This occurs when hard pitch has to be softened by the buyer to make it more suitable for the manufacture of patent fuel. For this purpose special *pitch-revivifying apparatus* have been constructed. Such an apparatus, as employed at the Blanzy coal-mines, is described in Payen's *Précis de Chimie industrielle*, 1878, ii., p. 919, as follows:—In Fig. 131, C is an upright boiler, 6 ft. in diameter, 9 ft. 2 in. high, holding about 320 cub. ft., and provided with a steam-jacket. In the centre revolves an endless screw, V, surrounded by an annular casing, which is heated by steam entering at *f* and issuing at *h* into the outer jacket; the condensation-water is discharged by *r*. At the bottom are the annular gratings G G (made of perforated iron plate) for retaining large pieces, the pipe S for discharging the revivified pitch, and a cleaning-hole (*t*). The boiler C is surmounted by a wrought-iron chamber, D, of equal size, to receive the froth formed during the operation. Here is a manhole, T, and a gland for the passage of the screw, V. The work is carried on in this way:—A certain quantity of tar, creosote oil, or the like, is let into the apparatus through the pipe *k*; steam is admitted till the heat rises to 150°; the screw is made to revolve; and the pitch which is to be revivified is gradually charged through the manhole T. More tar and pitch are added until the boiler contains about 9 tons of materials. The plate P prevents the pitch thrown in at T from falling upon the screw. The pitch is soon melted in the hot tar; the mixture passes through the sieve G, is lifted by the screw V, and thrown out again on the top. After eight hours all is melted and homogeneous; now the discharge-cock is opened and the revivified pitch run into coolers, after which the operation can be commenced anew.

The revivification can be effected by means of creosote oil, naphthalene, or tar which is merely deprived of the light oil (= asphalt, *supra*, p. 451). It has been found at Blanzy that the creosote oil does not modify the agglomerating property of pitch, but merely renders it more liquid; naphthalene increases the agglomerating property, but causes solidification at too low a temperature; best of all is tar deprived of light oils, of which 10 or 20 parts are taken for 100 of pitch. (Prob-

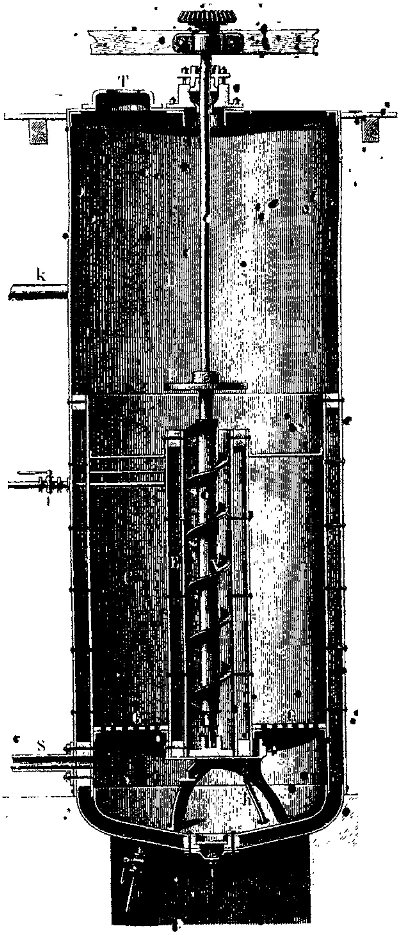

FIG. 131.

ably the last tar-oils, deprived of anthracene, would be still better.)

W. J. and A. Malden (B. P. 12230, of 1907; Fr. P. 387674) state that they improve the tenacity and raise the softening point of (tar and) pitch by the following treatment. They liquefy the material first moderately, so as to prevent the evaporation of oils, say to 50° or 60°, add to it 10 per cent. of manganese peroxide, with which the liquid substance is well mixed, then 5 per cent. of sulphuric acid of sp. gr. 1·84, and heat up to about 180° C. At this point the temperature is maintained, until the evaporation is equal to about ¼ per cent. in the last fifteen minutes of the treatment, whereupon the mass is allowed to cool. By this treatment the softening point is raised to such an extent that the disadvantages arising in the use of briquettes made in the ordinary way do not occur.

Applications of Pitch.

Coal-tar pitch is applied for many industrial objects, partly in the solid state, and partly dissolved in oils (regenerated tar, tar varnishes, iron cement, etc.), on account of its reducing-properties, its suitability for cementing substances in the shape of powder, of its insulating-properties for electricity, heat and moisture, etc, etc. As a *reducing agent* in chemical processes it is mostly too expensive, but it is used (as hard pitch) in the manufacture of ultramarine.

The Manufacture of Patent Fuel (Briquettes).

The principal employment of coal-tar pitch is for making *patent fuel* (*briquettes*) from small coal or coke-breeze. A detailed description of this industry does not come within the scope of this work; a number of special treatises have been written upon it, as the French one by G. Franquoy (1860) and the German ones by Gurlt (*Die Bereitung der Steinkohlen-briquettes*, Braunschweig, 1880), by Jünemann (*Die Briquette-industrie*, Hartleben's Verlag), and by Preissig (*Die Presskohlen-Industrie*, Freiberg, 1887); and the technical cyclopædias also contain much information upon this subject, of which we shall only give the outlines here.

This industry would appear to be due to Ferrand and

Marsais, who in 1832 obtained a French patent for employing coal-tar for this purpose. Marsais after 1842 employed soft pitch, and in the same year founded the works at Berard, near St Etienne. Hard pitch was used in 1843 in England by Wylam, and since 1854 in France. The patent fuel made near St Etienne was sold by the name of "péras."

The manufacture of patent fuel is the most natural outlet for the immense quantities of small coal (slack, duff, etc) obtained at the majority of coal-pits, and saleable only at a very low price, or sometimes not at all.

For Germany we quote the production of the chief district, that of Rhineland—Westphalia, as shown by the Dortmund producer's union.

Year.	Briquettes produced.	Average price per ton.	Pitch consumed	Average price of pitch at works.
	Tons.	Mark.	Tons.	Mark.
1894	754,414	8·82	60,785	43·75
1895	796,363	9·07	59,032	45·50
1896	830,980	9·34	65,067	43·00
1897	943,732	9·90	70,631	35·35
1898	1,078,338	10·22	79,757	30·75
1899	1,295,113	10·66	103,485	34·00
1900	1,530,816	12·27	108,976	42·50
1901	1,563,928	13·33	116,956	43·00
1902	1,610,215	11·20	112,795	42·00
1903	1,780,390	11·47	113,923	54·50
1905	2,152,000	...	...	...

According to Bock (*Z. angew. Chem.*, 1908, p. 2520), that district in 1907 produced 2,800,000 tons of patent fuel.

The total production of patent fuel in Germany in 1909 was 5,151,849 tons (value 76 millions mark); in 1910, 5,617,259 tons (value 74¼ millions mark).

In France the production of patent fuel in the year 1887 amounted to 1·2 to 15 million tons, and about the same up to 1900. The production of the two most important French coal districts during more recent years has been (in tons):—

	In 1905.	In 1906.	In 1907.	In 1908.
Pas de Calais . .	412,491	357,981	450,547	507,510
Nord	559,638	580,352	740,750	832,307
Together .	972,129	938,333	1,191,297	1,339,817

In Belgium (according to the Annuary of the Oberbergamt Dortmund) the production has been:—

	Tons.		Tons.
1901	1,578,800	1905	1,711,920
1902	1,616,520	1906	1,887,090
1903	1,686,415	1907	2,040,670
1904	1,735,480	1908	2,311,210

England and Scotland produced already before the year 1900 a million tons of patent fuel, of which 850,000 tons were exported, principally to Italy. The production of recent years, according to the *Jahrbuch*, ix., p. 738, was:—

	Tons.		Tons.
1905	1,604,649	1907	1,600,000
1906	1,573,220	1908	1,604,648

Austria-Hungary, according to Kosmann, produced before 1890 about 50,000 tons per annum. The production of patent fuel in Hungary alone was:—

	Tons.		Tons.
1904	103,000	1906	152,000
1905	145,000	1907	155,000

Spain (according to the same source) produced:—

	Tons.		Tons.
1903	322,978	1906	311,328
1904	307,630	1907	355,718
1905	290,830		

The United States produced:—

	Short tons.
1907	66,524
1908	90,358
1909	139,661

Briquettes are also manufactured in Russia, China, India, and other countries.

The total production in Europe was estimated by Kosmann at about 4 million tons; at the present time it amounts to at least 10 million tons, corresponding to 750,000 tons of pitch.

Schorr (*Eng. and Min. J.*, lxxxix., p. 520) states that in the whole world the production of patent fuel of all descriptions had risen from $4\frac{3}{4}$ million tons in 1885 to 26 million tons in

1909, in the first line by the rapid extension of this industry in Germany.

The *raw material* for the manufacture of briquettes is usually small coal of non-caking quality, but sometimes also coking-coal, from which the coarser particles (from ⅛ to ½-in.) are removed by sifting, whereupon the remaining small coal is purified and finely ground. It is then *agglutinated* in most cases by coal-tar pitch, experience having shown that only this cementing substance can be procured in sufficient quantity, at reasonable prices, and most successfully. It increases the heating-power of the briquettes, and, moreover, protects them during a long time of storage from falling to pieces, and from loss of quality and weight. Many patents have been taken out for replacing coal-tar pitch for this object by the syrupy mass obtained by the evaporation of the waste liquor from the manufacture of wood pulp, but this mass has the drawback of containing a good deal of sulphur, and of being partly soluble in water, so that the briquettes made by it deteriorate when being stored in the open air, as is usually the case.

The *quality of the pitch* (*cf.* also *supra*, p. 534) used for making briquettes is of great importance. "Hard pitch" is not suitable for this purpose, no more than soft pitch. Quite generally a middling hard pitch is used which, according to Spilker (*Kokerei und Teer-produkte*, p. 47), ought to have the following properties:—

1. The percentage of ashes ought not to exceed 0·5 per cent.

2. The softening-point should not be below 60°, nor above 75°.

3. From 70 to 75 per cent. of the pitch should be soluble in aniline and pyridine bases.

4. The residue from coking the pitch should not be above 45 per cent.

Bernus (*Bull. Soc. Chim. Belg.*, 1911, pp. 7 *et seq.*) has made an extensive investigation of the nature of coal-tar pitch with reference to its suitability for the manufacture of briquettes. According to him pitch consists of (1) coaly substances which possess no agglutinating property, and which remain behind when treating the pitch with organic solvents. This so-called "free carbon" contains carbon, hydrogen, and oxygen; it is prejudicial in the manufacture of briquettes. (2) Agglutinating and plastic substances, which are the active part of the pitch in that manufacture. They differ from the coaly substance by their solubility in carbon disulphide and carbon tetrachloride. At ordinary temperatures they form a solid, black mass, with a shining surface which softens on heating, and at 180° forms a strongly agglutinative, tough liquid. On heating it to 300° in contact with air, there is no increase of weight, but its plasticity is gradually reduced, part of it being transformed into a black mass insoluble in carbon disulphide, another part remaining unchanged. Bernus distinguishes in the agglutinating and plastic constituents of pitch two groups: (*a*) those which remain unchanged on heating upwards of 300° during some time, retaining the solubility in carbon disulphide; of these there is 75 to 85 per cent. present. This substance is a reddish-brown mass, passing over at 45° to 60° into a tough, viscous liquid, and consisting of a series of hydrocarbons which are partly precipitated by picric acid. They are the active agglutinant in the manufacture of briquettes. (*b*) The substances, which on heating above 300 become insoluble in carbon disulphide, forming from 15 to 25 per cent. of the mass. These are soluble in ether and acetone, and on evaporation of the solvent appear as a crystalline, shining, black powder, which, on heating, swells up and becomes insoluble. They are "unsaturated" compounds, as their solution absorbs bromine. The proportion between coaly and plastic substances is illustrated by the following analysis of a Belgian and an English coal-tar pitch:

	Belgian Pitch.	English Pitch.
Coaly substances .	45·67 per cent.	27·98 per cent.
Plastic substances:		
(*a*) saturated hydrocarbons .	43·13 ,,	56·79 ,,
(*b*) non-saturated hydrocarbons .	11·20 ,,	16·84 ,,

The proportion of "plastic substances" in the pitch determines the amount of pitch to be used for agglutinating the coal.

The keeping-property of the briquettes depends, moreover, on the amount of pressure and the speed of the blows in the moulding machine. If the pressure is too low, the solidity of the briquettes is impaired. But if the blows are too rapid, the air present in the mixture has not enough time for escaping, and a number of extremely thin layers of air is formed which prevent the adhesion of the coaly particles. Very dry coal naturally requires more agglutinating-substance than bituminous coal. Damp coal is less suitable than coal free from water.

The selling price of briquettes is usually the same as that of lump coal, sometimes higher. They are mostly made in prismatic forms, sometimes in the shape of cylinders, balls, or the like, and especially of perforated bricks. The weight of each brick is from 33 lb. down to 1½ oz. The specific gravity ranges from 1·10 to 1·40.

Good briquettes ought not to weigh above 22 lb., and should possess the crushing-strain of natural coals. For this purpose they must contain at least 5 per cent. of pitch if very strongly pressed, or 7 to 8 per cent. if made with less pressure. They must not leave more than from 6·5 to 6·75 per cent. of ashes if intended for locomotive use, or 10 per cent. if for steamboat use. Their regular parallelopiped shape permits easy stowage in the bunkers. The loss in transit by disintegration is only 1 or 2 per cent., against 30 to 50 per cent. in the case of coals. They ought not to fall to pieces in the fire. Good patent fuel has 10 per cent. more heating-power than good steam-coal; it makes much less dirt, and, if manufactured with hard pitch, it produces less black smoke than most descriptions of coal. A very important advantage of patent fuel is, that the fireman knows exactly how many pieces he has to put into the furnace at certain intervals in order to produce a certain effect, and that the foreman or manager can estimate whether this has been done by a single glance at the briquettes stacked beside the furnace.

Briquettes are mostly made with moderately soft pitch, but it should not be too soft. Briquettes made with hard pitch give less black smoke than the coal they are made of, according to experiments made at the German Imperial Wharf at Wilhelmshaven between 1874 and 1886. If hard pitch is to be used for this purpose, it must be ground and the mixture brought to a higher temperature; the injurious action upon the eyes of the workmen is a great drawback in this case. (Cf. *supra*, p. 364.)

Non-bituminous coal naturally requires a greater addition of pitch than bituminous coal.

Briquette-moulding Machines (*presses*).—Some presses have closed and others open moulds, the latter either with direct or indirect action. In Mazeline's direct-action press, the steam-cylinder piston on rising forces, by means of a one-armed lever, the press-ram from below into the moulds, which are contained in a circular platform, revolving by means of a ratchet. The finished briquettes are forced out by the rams sliding along an inclined plane. The ratchet arrangement is liable to frequent breakage. In the indirectly acting machine of Middleton and Décombay the pressure is caused by an angle-lever carried down by a weight; the finished briquette is forced out by another angle-lever. Here also the platform is turned round by a ratchet arrangement. In the similar machine of Hanrez, the lever causes pressure at the same time from above and below, limited by a hydraulic ram; the forcing-out is effected by an inclined plane, the revolution of the platform by a ratchet. In Durand and Marsais's machine (especially adapted for smaller work) the ram is pressed into the mould by an eccentric sheave; afterwards by a similar sheave the closing-plate is removed and the briquette pushed out. Another similar machine has been constructed by Biétrix.

In the case of machines with open moulds, the pressure is obtained by the friction of the mass at the conical mouth of the press. Hence they require more power than those just described, but do more work; they are as yet employed exclusively with soft pitch.[1]

In Everard's machine the tubular moulds are arranged radially in a circle, so that the eccentric attached to the vertical working-shaft can by turns force the rams in and out of the moulds. At every back stroke of the ram a fresh mass is forced into the mould, which by the forward stroke is pressed against the old mass and forces this out of the open end of the mould. A similar machine, by Bouriez, permits the use of hard pitch also. Revollier's and Mazeline's machines are worked by hydraulic pressure.

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[1] The latter process is exactly analogous to that of moulding bricks—the machines that work for dry clay being constructed with closed moulds, those for wet clay with conical mouthpieces (dies). But it is well known that the former take much more power and have a much larger output than the latter. Is the opposite really the case with patent-fuel presses?

Of other patents for manufacturing patent fuel we will mention:—E. F. Treddar (Ger. P. 16017); G. H. Lenk and W. H. Lehmann (Ger. P. 15789); G. J. P. Couffinhal (Ger. P. 15239); M. Neuhaus and O. Henniges (Ger. P. 18538); S. Butler (B. P. 7791). Bowing (Ger. Ps. 51099 and 58708) goes back to tar itself; also the Aktien-Gesellschaft für Teerprodukte (Ger. P. 63648), Jenker (Ger. P. 61166), and Bergmann (Ger. P. 101299). G. S. and C. Cory (B. P. 7772, 1884) mix 7 parts pitch with 1 part naphthalene.

Bornemisza and Kopal (Ger. P. 31644) make a kind of artificial fuel by mixing 100 parts of melted coal-tar pitch with wood-cuttings or other vegetable refuse, allowing to cool down on stone slabs, moulding into pieces 4 × 2 in., with a central hole, coking these pieces, putting on an iron rod, within a wire-gauge cylinder contained in an ordinary gas-retort, and pressing the product once more while still hot. Hüttemann and Spieker (Ger. P. 86827) make briquettes with a mixture of 3 or 4 per cent. pitch and 1 per cent. rosin.

Schnauder and Bergmann (Ger. P. 101299) mix finely ground coal or coke with two or three times its weight of melted pitch. This mixture, moulded into blocks, is to be used like ordinary pitch in the manufacture of briquettes; it is asserted that it possesses the same binding powers, and does not so easily soften in warm weather.

The employment of coke-breeze for the manufacture of patent fuel is strongly recommended in the *J. Gas Lighting*, 1909, pp. 82 *et seq.*, and in Herring's booklet, *The Design, Construction, and Equipment of the Granton Gas-works*, where the manufacture of very small egg-shaped briquettes, weighing only 4 oz. each, and specially intended for domestic fires, is described.

Sonnenschein and Köhler (Ger. P. 221072) surround the briquettes with paper soaked with a solution of water-glass, ammonium sulphate, borax, or alum, to render it less combustible, in order to prevent the briquettes from burning too quickly and falling to powder.

Conring (Ger. P. 108197) makes briquettes by heating 1870 parts ground coal to 150°, 80 parts pitch to 160°, intimately mixing them together, adding milk of lime made from 50 parts lime, and working it all up in a press.

Schöndeling (*Z. angew. Chem.*, 1906, p. 348) reports on the employment of Bohemian lignite for the manufacture of briquettes.

Plate & Lieb (Ger. P. 164291) prescribe the use of *wet* coal (not below 10 per cent. water) and subsequent heating of the briquettes to 100° C., which causes the pitch to be very finely divided by the steam, and therefore permits reducing the amount of pitch to only 3 per cent.

Pauline Grayson has obtained a German patent (No. 163367) for a very remarkable mixture: 6 per cent. gypsum, 16 lime or cement, 20 water, 12 mineral oil, 6 pitch or rosin, which leaves only 32 per cent. for coal!

H. S. Robertson (B. P. 20281, 1906) for the manufacture of artificial fuel, mixes a tarry substance with hydrocarbon oil, removes the precipitated solid matter, and employs the fluid as a solvent for resinous matter, with or without the addition of tar and common salt.

Schmetz & Schramm (Ger. P. 141344) make briquettes with smaller percentage of pitch than is otherwise required, by melting hard pitch with 60 per cent. of coal powder, passed through a sieve with from 50 to 250 meshes per superficial centimetre. Of such coal, up to 60 per cent. can be incorporated with the pitch.

Epp (Fr. P. 470136) heats clay and sawdust in a steam-heated mixer, adds coal-tar and previously boiled pine-resin, then nitric and sulphuric acid, moulds the cooled mixture, and exposes it to the atmosphere for one or two days. An alternative process consists in using clinker or ashes with finely divided pitch, tar, and sulphuric acid.

Behr (*J. Gasbeleucht.*, 1915, pp. 110-113) describes in detail the manufacture of briquettes from coke dust.

J. Armstrong (B. P. 1188, 1914) describes an automatic moulding apparatus for briquettes.

Testing the Quality of Briquettes.

The tests usually made at the patent-fuel works are very uncertain. The makers try the *hot* briquettes, as they come from the press, for their resistance by hand, or by dropping them from a height of 6 or 9 ft. on to a stone floor. This is very deceptive; briquettes made with pitch of 50° or 55° softening point thus seem to be less resistant at 75° than those made with harder pitch (70° to 75° softening point); but in the *cold* the former are really harder than the latter. That test is also influenced by the amount of pressure and the violence of the blow.

Le Ray (*Chem. Centr.*, 1900, ii., 1298) estimates the quantity of pitch contained in the briquettes (which should be about 8 per cent.) by grinding up a sample with five to ten times its weight of coarse sand, and treating in a Soxhlet extractor with a mixture of equal parts of petroleum spirit and disulphide of carbon.

J. E. Mills (*Oil, Paint, and Drug Reporter*, 1908, 17th to 27th July; *J. Soc. Chem. Ind.*, 1908, p. 887) describes the experiments carried out at the United States Government fuel testing office at St Louis for determining the relative values of the various binding agents for briquettes, among which, of course, tars and pitches from coal hold a prominent place.

This subject is treated in detail by Constam and Rougeot in *Glückauf*, 1906, pp. 406 *et seq.*

The testing of the pitch intended for making briquettes will be described at the close of this chapter.

Varnishes made with Pitch; Refined (prepared) Tar.

A very rational employment of coal-tar-pitch is for making varnishes, for iron especially, but also for wood, etc.—of course all of them black. They are made in a very simple way, by melting pitch with various products of tar-distillation, and hence require no admixture of any foreign matter. No plant is necessary but an open pan set in a covered place, so as to be heated from without; but it is certainly preferable to employ a closed pan with a mechanical agitator. The melting-pan may be made either of cast- or wrought-iron; but it is best made of the latter, because then no cracking (very dangerous in this case!) can occur. It may be an upright cylinder with convex bottom, or a horizontal boiler. For working on a large scale, a mixing-apparatus like that represented in Fig. 131, p. 538, is preferable.

In this pan the whole quantity of pitch to be worked up is melted along with a little of the oil to be employed, which promotes the melting of the pitch and prevents its speedy solidification. Still the temperature will rise pretty high before all the pitch is melted, and it is best to let it cool down a little, lest the oils now added should be raised to the boiling-point, which will, of course, most readily happen with light oil or naphtha. But the cooling must never be allowed to go so far that some part of the mass begins to solidify. Now the remainder of the oil is added very gradually, stirring each portion completely into the mass. From time to time a sample is taken out and cooled, to see whether the proper consistency has been attained.

The commonest kind of varnish is made in the manner just described, from pitch and creosote oil. In this case even a simpler process may be followed. The tar is distilled (if need be, in a separate small still) till the light oil has passed and heavy oil begins to pass, or till all the "middle oil" has passed over, say up to 240°. The fire is now drawn out, the still allowed to cool down a little, and the residue ("asphalt") diluted within the still itself with the necessary quantity of creosote oil, say ¾ of the weight of the pitch, after which it is run off in the liquid state. Or else the distillation is carried on to hard pitch, in order to obtain the anthracene; the heavy oil, freed from anthracene and, if possible, from naphthalene, is run in till the necessary degree of thinness is attained; and the mass is well mixed. We have described this process above, pp. 469 *et seq.*, as it is carried out within the stills themselves; but sometimes the creosote oil is mixed with the hard pitch in the pitch-cooler, a pipe conducting it from a store tank into the fluid pitch within the cooler. The varnish thus obtained, in England called *refined tar*, in Germany known as *prepared tar* or *artificial Stockholm tar*, is less valuable to the tar-distiller than raw tar, since the more valuable components—benzol, phenol, anthracene, and partly naphthalene—have been removed; on the other hand, it is much more valuable than raw tar for many purposes—as a paint, for the manufacture of roofing-felt, or roperies, etc. It penetrates much more quickly and deeply nto wood, stone, etc., than raw or even boiled coal-tar, and dries nuch more quickly, even more so than wood-tar (real Stockholm ar). For making dust-free roads it is also much better than aw tar, *cf.* pp. 361 *et seq.* It is greatly to be recommended for lkali and other chemical works, for painting any wood-, iron-, r stone-work needing protection against acids, chlorine, etc. Such prepared tar is especially very much to be preferred to oiled tar for painting iron (where raw tar, owing to its ammonia, s quite inadmissible), as it dries both much more quickly and vithout leaving cracks, and forms a good, shining coat. The lrying takes from twelve to twenty-four hours, according to the veather. As this sort of varnish forms a pretty thick coat, it is nly applicable to coarse ironwork, but is excellent for this.

Most of the "refined tar" is used in the manufacture of oofing-felt, a great deal also for the manufacture of the basic ining of the converters in the Thomas-Gilchrist steel-making rocess.

Disputes concerning the quality of "refined tar" have made t desirable to possess *methods for testing the quality* of that ubstance, in a proper manner. Such methods have been vorked out by myself (Lunge, *Z. angew. Chem.*, 1894, p. 449), nd have been found to be very useful in practice. They omprise the following operations:—

1. Estimation of *specific gravity*, as described on p. 520.
2. Estimation of *viscosity* (*vide supra*, p. 526).—The ordinary instruments for this purpose, based on measuring the velocity of issue from a small orifice, cannot be employed in this case, as the apparatus would be too difficult to clean. The instrument described below, based on the velocity of immersion, obviates this difficulty and, although not scientifically accurate, is altogether sufficiently so for practical purposes.

Lunge's "tar-tester," as shown in Fig. 132, somewhat resembles a hydrometer, but is made of very strong glass, in order to allow its being easily cleaned. For the same reason, but chiefly for the purpose of a more uniform velocity of immersion, the lower part is made without the ordinary contraction and bulb, of cylindrical shape with a semicircular end. The following dimensions have been found to answer the purpose:—Length of lower parts, inclusive of the upper and lower ends, 100 mm., outside diameter 20 mm. Length of upper part 225 mm., outside diameter 8 mm. Beginning of scale 15 mm. above the conical end of the lower part. Length of scale 190 mm. The lower point of the scale marks the specific gravity 1·400; the top of the scale 1·050. The point 1·250 is 81 to 83 mm. above the end of the conical portion. Weight 39 g., with a margin of ± 0·5 grm.

The manipulation of the tar-tester is as follows :—The tar is poured into a glass cylinder which, after immersion of the tester, must be as nearly as possible full, to facilitate the observations. The tar is stirred with a wire bent at the bottom into a ring, and its temperature determined to 0°·5 C. The observations should be made at 15° C., and the cylinder must be brought to this temperature by placing it in a water-bath, with frequent stirring. The tar-tester is now suspended above the cylinder, preferably by means of a spring-clamp. It is immersed exactly to point 1·250, taken out and allowed to drain for three minutes, suspended as above. Only then the proper observations begin. A seconds-watch is taken in one hand, the tester in the other, so that its bottom just touches the surface of the tar, and when a full minute is reached the tester is allowed to drop. It will at first fall very quickly, until the wider part is reached, afterwards but slowly. If it assumes a slanting position and touches the side of the cylinder, it must be righted by a gentle push. Directly the point 1·250 has been reached, the number of seconds is read on the watch, the tester is taken out and is allowed to drain for two or three minutes before making the next observation. Three or four, or even more, tests must be made, and they should not differ by more than two or three seconds.

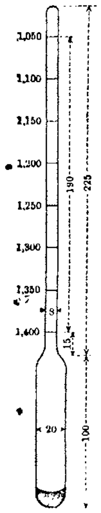

FIG. 132.

Of course the specific gravity of the tar can be taken by means of the same instrument; but for estimating the viscosity the point 1·250 should be observed, because the last sinking takes place much too slowly.

Apparatus for estimating the viscosity of tar and tar varnishes is also described in the Ger. P. 244098, of Dr Paul Meyer Aktien-Gesellschaft, of Berlin, and in the B. P. 22042, of 1911, of J. Hutchinson.

3. Estimation of the *volatile constituents*.—This cannot very well be performed by an ordinary distillation. The following method seems rather more complicated, but is decidedly preferable, as it yields uniform results, as I have ascertained. One hundred grams of the tar is distilled from a tubulated retort of refractory glass, protected by asbestos paper, until a certain quantity of liquid has passed over into a graduated cylinder. The specific gravity of this distillate is ascertained, as well as that of the pitch remaining in the retort (after allowing this to cool and breaking it) and the softening point of the latter, as described later on. If the first experiment does not yield proper pitch of medium hardness, a second and, in case of need, a third experiment, with more or less distillate, must be made.

In buying and selling refined tar, distinct conditions should be stated for the specific gravity, viscosity, and minimum quantity of distillate. The last and most troublesome test can usually be omitted, as the two former will suffice for most purposes. We cannot here quote special figures, since for various purposes different conditions will be required.

Church (*J. Ind. Eng. Chem.*, 1911, p. 229) tests "prepared" and "distilled" tar, intended for road-making, painting and dust-preventing, for its specific gravity, its contents of "free carbon" (as described *supra*, pp. 308 and 523), and its viscosity. This he estimates in the case of thin tars by means of Engler's viscosimeter (employing 60 c.c. of tar at 60°), in that of thick tars, up to soft pitch, by means of Schutte's penetrometer, the bolt of which should for this purpose have a diameter of ⅝ in. and a length of 1 in. The distillation of the tar he carries out exactly as prescribed in the case of creosote oil (*vide infra* at "impregnating-oil") by the standard method of the "creosoter." *Cf.* also what is stated for road-tarring, pp. 361 *et seq.*

Examination of tar-varnishes for their quality as protectors of iron against rusting (Volger, *J. Gasbeleucht.*, 1912, p. 19).—Pieces of sheet-iron, about 0·5 mm. thick, 10 × 30 mm., scoured clean on one side, are painted with the tar-varnish on both sides. This paint should be laid on easily and should not dry in the brush while being used; the drying-time should last at least two or three hours. When the first coat of varnish has dried, a second coat is laid on. After lying for three or four days, a trial is made of the *elasticity* of the varnish, by bending the sheets in many directions; this should not cause the varnish to be cracked or to break off. For testing the *rust-protecting quality*, a second sheet, painted as just described, is suspended for about a month in vessels containing ammoniacal gas-liquor or other acid or alkaline liquids with which the painted plates may come into contact; this ought not to produce any blistering of the paint. Now the paint is carefully taken off with the aid of benzol, and the clean sheet is examined for any rust spots. In order to establish the injurious presence of any ammonia (which would indicate an admixture of raw tar), a few cubic centimetres of the varnish are heated in a test-tube, and a strip of moistened red litmus paper is held over the tube; this paper should not turn blue.

A better kind of varnish is obtained by melting pitch with light oil in the above-described manner. For this purpose not the light oil distilled from the tar, but the last fraction from the light-oil still, or the oil taken away from the carbolate of soda (*cf.* Chapter IX.), is employed, which is deprived of its more valuable components. For 100 parts of moderately hard pitch about 60 parts of light oil may be calculated. This varnish gives a more lustrous and smooth surface than the former, and leaves a much thinner coat. Its drying-time varies from four to six hours; and it can be employed for finer ironwork.

Lastly, more quickly-drying and thinner varnishes can be obtained in all gradations, by substituting naphtha for part of the light oil, either the commonest burning-naphtha being employed, or else some made on purpose by carrying on the rectification of benzol by steam beyond the usual termination. The rule is, first to work up all the light oil with the pitch, and then to add the naphtha, keeping the mixture as hot as is consistent with the volatility of the naphtha. Besides, very thorough and long-continued stirring is necessary, since naphtha is not so easily incorporated with the varnish as the heavier oils, and the varnish would otherwise be very likely to separate into a black deposit with naphtha floating on the top. It is possible by means of very common naphtha to make varnishes that dry in an hour, or even in a quarter of an hour, which can be employed for any kind of hardware in which blackness is of no consequence.

All three kinds of varnish adhere firmly to iron, and after drying exhibit a considerable degree of hardness, together with glossy lustre and smoothness, and more of the latter in the case of the better descriptions.

A patent of Marchisis and Stevens (23rd Sept. 1870) seeks to improve such varnishes by heating with bleaching-powder or a solution of common salt and washing with copperas solution. Whether this does any good we cannot tell.

Chaumont[1] makes a varnish for wood and metals by dissolving 300 parts of coal-tar asphalt in 100 carbon disulphide. In lieu of such asphalt, natural bitumen or rosin may be employed. The materials are brought together in a closed vessel, to prevent the evaporation of the carbon disulphide. In twelve to twenty-four hours the varnish (the smell of which will hardly recommend it) is ready for use.

Watson Smith (priv. comm.) recommends as a good varnish for tarpaulins one obtained by melting wood-tar pitch with the same weight of coal-tar cresote oil, freed as much as possible from naphthalene; also as a good metal-varnish one obtained by melting 6 lb. of dark rosin with a pint of boiled linseed oil and a gallon of creosote oil, to be mixed, for finer work, with a little gum and any kind of colouring-matter.

E. Heusser (Ger. P. 24231) extracts pitch with warm light tar-oil or benzoline. A solution is formed which, on evaporation, leaves a mass resembling native asphaltum. The residue left after extraction forms a black paint of great covering-power.

Roth (Ger. P. 152758), prepares a protecting compound from 33 parts heavy oil, 20 parts light oil, 47 parts pitch and aluminium oleate, which is sold by the name of "inertol," and is specially recommended for protecting iron and cement under water, such as in brick-tanks for drinking-water.

A German patent (86345) was obtained by the Aktien-Gesellschaft für Teer- und Erdöl-Industrie for an asphalt compound, to serve as a protection of wrought-iron water-pipes against corrosion. It is sold by the name "Cumanollack."

According to G. Kraemer (priv. comm.), a good varnish is obtained from oil-gas, tar-pitch (which contains but a few per cent. of free carbon), heavy benzol, and small quantities of crude carbolic acid.

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[1] *Wagner's Jahresber.*, 1865, p. 686.

The Aktien-Gesellschaft für Asphaltierung und Dachbedeckung vorm. Joh. Jeserich manufactures a varnish for painting iron, specially valuable by its permeability, by fusing oil-gas tar with goudron and brimstone, which is sold with the designation "siderosthen."

Nöthling (*Jeep, Der Asphalt*, Leipzig, 1899, p. 253) dissolves 24 parts coal-tar pitch in 36 parts benzol on the water-bath, and allows the solution to settle at 15° to 20°. To the liquid, separated from the deposit, he adds a solution of 2 parts elemi rosin and 1 part copaiva balm in benzol, and, if needed, some benzol, until the mixture is of the proper quality for painting. Ten parts of dehydrated tar are boiled, and 2 parts of graphite and 1 part of red lead added; the mixture is heated to boiling, and to it are added 1 part flowers of sulphur and 2 parts ignited powdered pumice stone.

The *Chemische Fabrik Gross-Weysandt* (Ger. P. 122688) treats oil-gas tar with chloride of sulphur (S_2Cl_2) and dissolves the product in appropriate solvents.

The pure bitumen of pitch, freed from fixed carbon, as it is obtained by extraction (*vide infra*) is an excellent material for the preparation of superior tar varnishes.

Asphalt, Asphalt-paper, Roofing-felt, etc.

The term "asphalt" was formerly restricted to what is now called "natural asphalt" or "bitumen," of which in 1901 the United States produced 63,134 short tons, and Sicily exported in the same year 62,770 tons. This substance is principally used for street-paving in various forms, and cannot for this purpose be entirely replaced by the product from coal-tar, to which the name of "asphalt" is also given. A very instructive series of papers on natural asphalt is found in the *Chem. Trade J.*, 1902, xxxi., pp. 184, 207, 228, 252; and in *Baumaterialienkunde*, 1906, xi., p. 12 (by Malenkovic). In this book, of course, we use the word "asphalt" as denoting a product obtained from coal-tar.

Marcusson and Eickmann, in the *Chem. Zeit.*, 1908, No. 80, discuss the processes for distinguishing natural asphalt from the products made from tar, petroleum, etc.; these always contain paraffin, which is absent in natural asphalt.

Professor Holde demands that the expression "asphalt" should be restricted to such natural asphalts which are almost entirely soluble in benzol and contain from 1·5 to 10 per cent. of sulphur, as employed for building purposes, for preserving materials against humidity, for making varnishes, etc. Materials obtained artificially in the distillation of coal-tar, petroleum, etc., and used as surrogates for natural asphalt, ought always to be denoted in such manner that no confusion with natural asphalt can take place.

Asphalt, both that obtained directly in the distillation of coal-tar and that made by mixing pitch with heavy oils and with solid substances, is useful for many purposes. It is employed for keeping the subsoil moisture from metal pipes, iron tanks, etc., sunk in the ground. For this purpose the semi-liquid mass is mixed with sand, ashes, etc., into a lumpy paste, of which a thickness of 4 or 6 in. is employed. We shall quote particulars of such mixtures below.

Such asphalt, made direct from tar, is not so frequently used now as formerly; but similar mixtures are artificially made, by driving off all the creosote and anthracene oil, and pumping back the heavy oils, meanwhile freed from their more valuable components, as phenol and anthracene, till the desired consistency of the residue has been attained. In this way is obtained not merely soft pitch, but also asphalt, and, with greater dilution, even "refined tar" or "artificial Stockholm tar" (p. 549) which is largely employed in the manufacture of roofing-felt (see below).

The employment of pitch or asphalt for *street-paving* is to be recommended in many respects. When used as a cement for joining the paving-stones, it makes the ground impermeable to the impurities from below and does not permit the passage of noxious effluvia. Tar-pitch is also used as a direct *substitute for natural asphalt*, but only in combination with the latter, for asphalting footpaths and for insulating foundation-walls from the ground-moisture. The mixture is melted in pans in the usual way; sand, brick-dust, ashes, chalk, and the like are added till the mass has become thick enough (for which purpose about the same weight of pitch will be necessary); the whole is well mixed, preferably by grinding in a pug-mill, and used hot. For footpaths the pitch is ground up with an equal weight of sandy or stony material, melted in a pan, and, before being laid down, is mixed with an equal quantity of gravel; so that the finished pavement contains about 30 per cent. of pitch. But it is not advisable to employ coal-tar pitch alone, without any natural bitumen; the latter is much more intimately combined with the earthy matters than the former can be. A mixture of the two is very suitable, and is cheaper than natural asphalt alone. In a similar way, moulded blocks are made from pitch and ground rock.

At some Scotch tar-works the pitch is run directly from the tar-still into a pug-mill, where it is intimately mixed with sand, sometimes also with chalk. From this mill the mixture, while still liquid, is run off into sand moulds to solidify. During the whole process, until the mixture becomes cool, offensive vapours are given off; the pug-mill or mixing-pan ought therefore to be covered with a hood, and the vapours carried away into a chimney-stack by means of a pipe. The space between the edge of the hood and the mill or pan should be enclosed by sacking which can be opened at certain places as requisite for manipulation. (Dr Ballard.)

Gobin (B. P. 1865, of 1878) melts 15 parts of bituminous shale with 35 parts of coal-tar pitch in a pan, till the froth which at first arises has subsided. Then he adds 10 parts of coke and 130 of limestone, both crushed, well mixed, and dehydrated by heating above 100°. Before cooling, he adds another 160 parts of gravel, well dried by heat. For street-pavements he increases the quantity of gravel up to 190 parts, moulds the mass into blocks of about 8 × 6 × 4 in., and lays these, like ordinary paving-stones, on a bed of gravel or sand.

Daguzan (Ger. P. 4999) mixes tar, first completely dehydrated by heat (probably he means "asphalt"), with previously "calcined," finely ground limestone or marble (quicklime?), 5 per cent. oxide of iron, potassium silicate, calcium sulphate, etc.

E. G. Williams (B. P. 13595, 1890) prepares asphalt, resisting acids and oils, by mixing sand with pitch, freed from creosote oil.

G. F. Sidney (B. P. 15316, 1896) heats tar or pitch during two to four hours to 350°, till the sp. gr. 1·261 has been reached, and then mixes it with ground schist or ashes.

The "Doerrite," described *suprà*, p. 364, might be mentioned in this connection as well. By the name of "Bithulic pavement." a composition is sold in Great Britain by the Northern Quarrite Co., in America by Warren Bros., in Germany by the Deutsche Quarrit und Bithulithic Pflaster Gesellschaft, which is manufactured by employing pitch as cementing agent, and has been extensively used. The exact composition of this article has not been published. Differing from tar macadam, it is prepared on the spot where it is used, because on transit it would cool down and become unworkable. The roads made from it are fit for heavy traffic, as reported by Powell in 1905 (*J. Gas Lighting*, No. 2207, p. 554). The apparatus costs £400. For a daily production of 31 tons of this mixture there is required 25 cwt. coal-tar, 4 cwt. tar-pitch, 5 cwt. coke, and 4s. total cost per ton of gravel, inclusive of capital interest and amortisation. Roads which formerly had to be repaired every third year now last seven or eight years, and are entirely free from dust and mud. Similar favourable results are reported from Germany. In France this process is carried out by the Société Générale de goudronnage des routes, 17 rue de Bourgogne, Paris.

The best tar pavement, according to communications from Mr S. B. Boulton, is made with refined tar (p. 549), or at least with thin tar-asphalt, in this way:—There is first a thin layer of concrete made, upon which is spread a mixture of tar with washed gravel free from loam. The gravel is thrown into a pan filled with hot tar; when thoroughly soaked, it is spread on the concrete and rammed down. After cooling, a top layer is formed, made of dry sand, hot tar, and a little pitch, in order to fill up the interstices between the gravel and produce a smooth surface. According to H. Riley,[1] macadamized roads are made in England as follows:—The material consists of slags and cinders from blast-furnaces and iron-mills, Yorkshire sandstone, Derbyshire limestone, and Leicestershire granite. It is crushed like road-metal and dried in furnaces or ovens. The tarry mixture varies in different localities. Some employ gas-tar and pitch, boiled together; others prefer a mixture of tar and creosote oil. The proportions differ according to the quality of the tar.

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[1] Quoted by Jahn, *Zeitsch. f. Transportwesen*, 1898, p. 329.

On the building of macadamized roads, using coal-tar and pitch as cement in England, Henry Riley makes the following statements:—The raw material consists of scoria and fluxes from blast-furnaces and iron-works, sandstone, limestone, and granite. These materials are broken up into pebbles, and the moisture is driven off by heating and the material used in this state. The substances used for cementing the pebble differ a good deal. Very much used is a mixture of pitch and gas-tar, boiled down to a certain consistency; sometimes creosote oil is preferred to the tar. The pitch should be hard, but not too brittle; the tar should be free from water, and preferably kept for some time. The proportion of tar and pitch must be varied according to the specific gravity and other properties of the tar.

At Gainsborough the proportions employed are to each ton of ballast 13 gall. of tar and 26 lb. of pitch. The ballast, dried on hot plates, is put into conical heaps, the tarry mixture is poured on and is worked through until each stone is thoroughly covered. It is preferable to leave the mixture lying for a month or two, covered up, to give time for the tar to soak into the porous stones. A 4-in. layer of this is placed on the foundation and rolled down by a steam-roller; and a covering layer, 1 in. thick, is made of hard material, broken quite small and treated exactly like the former. At last the whole surface is sprinkled with limestone- or cinder-dust, and the street is blocked against traffic for about a week. This work should not be done during the winter months; the warmer the weather the more durable is this pavement, which costs about 8s. 6d. per ton, and which is extensively used in Great Britain.

Thenius (*Technische Verwendung des Steinkohlenteers*, pp. 117 *et seq.*) proposes mixing soft pitch with 10 per cent. of rosin oil, which is to make it more like natural asphalt, or with 50 to 60 per cent. of crushed limestone. This mixture is moulded into blocks, and is, with the addition of 25 per cent. of ground gravel or basalt, cast into mosaic plates for pavements, tables, etc.

Tar-asphalt can be considerably improved by the addition of *brimstone.* A. Winkler[1] adds to coal-tar asphalt (in the sense of the term adopted in this chapter) 5 per cent. of brimstone in small quantities, heating the mixture every time till no more sulphuretted hydrogen is given off. Probably in the heating, the sulphur decomposes the components rich in hydrogen, and thus renders the residue less fusible. Thus 75 per cent. of the tar is obtained as good asphalt, which does not soften in boiling water. A further proposal of his does not seem practicable, viz., to add 20 per cent. of brimstone to the tar before distillation; it is said that in this case only water and sulphuretted hydrogen escape during the heating, and good asphalt is obtained, equal in weight to the tar employed. The expense, the action of the sulphur on the metal of the stills, and the nuisance caused by the sulphuretted hydrogen, would be objections to this proposal.

A similar mixture is *Hausler's wood-cement*, well known in Germany as a roof-covering. This kind of roof is very much employed in Germany and Switzerland, being practically fire-proof, a bad conductor of heat, and almost indestructible. Thi cement is made of 60 parts dehydrated coal-tar, 15 pitch, an 25 brimstone. The mass should be kept from superheating, an the fumes discharged into the open air or under a hood, wher the sulphuretted hydrogen, going off in great quantity, cann injure the workmen.

G. Friedrich & Co. (Ger. P. 61555) assert that a mixture o various tars with pitch, rosin, brimstone, molasses, solution o indiarubber, etc., furnishes a wood-cement workable in th cold. Other modifications are Felten's "vegetable asphalt" an Rusch's "chlorite-cement"; but they do not appear to be rea improvements on the original.

Peterson-Kinberg, in his above-quoted book, p. 203, prescribes running 1500 litres of "refined tar" (p. 549) from th tar-still at a temperature of 270° C. into a mixing vessel, an quite gradually adding 6 litres of melted brimstone, continuin the agitation until all froth has disappeared.

Hannemann & Boisly (Ger. P. 83550) heat coal-tar pitc with sulphur, and treat the melted mixture with bleachin powder; after cooling, the mass is ground, mixed with som thickening stuff, and heated again.

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[1] *Chem. Centr.*, 1858, p. 337.

Asphalt Pipes, Insulating Masses, etc.

Coal-tar asphalt, or very soft pitch, is also employed for manufacturing *asphalt pipes*. This industry, introduced by Jaloureau, has been minutely described by Behrens.[1] Endless hemp paper, 7 ft. wide, is passed through a semicylindrical pan set in a furnace and filled with hot pitch.[2] A roller revolving in the pan takes up the paper soaked with pitch and conveys it to a smaller roller, forming the core of the pipe, round which about 100 layers of paper are wound. When the proper thickness has been obtained, fine sand is dusted on, and the whole is exposed to considerable pressure, which increases the compactness and homogeneity of the mass. After a short cooling in water, the core (which should previously be rubbed with soft soap) is drawn out by means of a crane, and the pipe is once more cooled by water. The joints of the pipes are made by iron flanges fixed upon them, or by thimbles formed of a wider piece of asphalt piping, and fastened on the pipe by a mixture of pitch and brimstone, or else by winding round them ten or twelve folds of linen cloth soaked in melted pitch. Similarly, any necessary elbow-pieces and bends are made, often at the place where the pipes are laid down.

According to the nature of the pitch employed, the pipes have different qualities, which must be taken into account in using them. If made with very soft, oily pitch, the pipes offer great resistance to the penetration of water, and hence are excellent for water-pipes in marshy ground. Those made of harder pitch offer a greater resistance to distortion by a higher temperature. Of course asphalt pipes can only be employed for conveying cold liquids or gases; but, with this restriction, they can be used for many purposes, both on account of their relatively low price and their valuable qualities. They are stated to resist a pressure of 33 atmospheres from within [?], and are sufficiently elastic for their joints not to break in case the ground settles down; they are not subject to be frozen up, being bad conductors of heat; they are not acted upon by dilute acids or alkalis, and can be laid in any soil. They are chiefly employed for conveying water, acids, air-blasts, for pit-ventilation; for covering underground telegraph-wires, for speaking-tubes, and sometimes for gas-pipes.

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[1] *Dingl. polyt. J.*, ccviii., p. 377.

[2] That Behrens does not mean real pitch, but either asphalt or very soft pitch, is apparent from the fact that paper would be partially destroyed at the melting temperature of hard pitch.

Such asphalt pipes and semicircular spouts made by cutting them in halves are excellent for carrying away waste liquors of an acid nature in chemical laboratories, and even in chemical factories, so long as they are not exposed to any heat.

Pipes of another kind are made from (probably harder) pitch by mixing it with gravel and casting it in moulds over a core of thin sheet-iron; the outside is covered with gravel, which is pressed or rolled in while the mass is still warm. The walls of these tubes must be very thick, as they are brittle. These pipes, manufactured by Chameroy, are extensively employed in Paris as water-pipes.

Doehring (Ger. P. 36666, 1885) has described a process for manufacturing pipes with a *glass core* and a jacket of paper, wood-cement, or soft pitch. Such pipes are resistant against liquids inside, and much more durable than glass tubes. They are made by the apparatus shown in Fig. 133, containing a winding-roller A and the wood-cement reservoir B, which is provided with a steam-pipe.

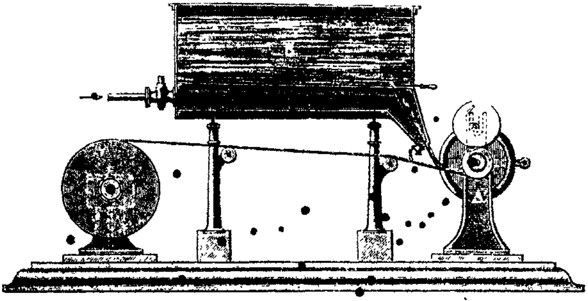

FIG. 133.

When using any kind of asphalt tubes, it must never be forgotten that they are liable to be distorted by heat.

Behrens (*loc. cit.*) also describes the manufacture of *asphalt paper* as a substitute for wax-paper. Ordinary wrapping-paper is wound off from a roller upon a heated drum, upon which a scraper is fixed. Melted pitch runs down in front of this to a depth of 1½ in. The paper thus covered with a thin film of asphalt runs over several rollers, and is ultimately wound round the last. Another kind of paper, consisting of a thin layer of pitch between two layers of paper, which is much used for covering damp walls, is made in a similar manner.

Another use of soft coal-tar pitch is for *insulating subterraneous cables*. These are laid in wooden shoots, afterwards filled with liquid pitch. For this purpose Lessing (Ger. P. 98278) prepares the pitch by dissolving it in suitable solvents and separating the solution from the solid portions which are good conductors of electricity; the pitch remaining after distilling off the solvent is a much better insulator than the raw pitch.

A German patent (No. 167166) by Rob. Muller describes the preparation of an insulating mixture from pitch and asbestos.

Mann (Ger. P. 170133) converts asphalt and similar substances into an emulsion by dissolving them in liquid solvents, treating them with soap and an appropriate colloid substance and recovering the solvent.

The Purification of Pitch by Extraction with Solvents.

We have mentioned *supra* that coal-tar pitch, along with bituminous substances soluble in carbon disulphide, benzol, etc., contains more or less insoluble matter, consisting of inorganic substances, and of "free carbon." These substances, being good conductors of electricity, impair the suitability of the pitch as an electrically insulating material. The following processes are intended to improve its quality in that respect.

Lessing (Ger. P. 98278) separates the insulating, soluble components of pitch from the insoluble conductors of electricity by treating the pitch with suitable solvents, *e.g.*, benzol, filtering the solution and volatilising the solvent by means of steam. The pure bitumen remains behind in the shape of a plastic mass, acting as a very good insulator, whilst the matters remaining on the filter can be used similarly to soot or retort-graphite in the manufacture of galvanic carbon. Practically the same process is described in the B. P. 6739, of 1901, of

L. Gaster; also in the Ger. P. 208600 of the Rütgerswerke Aktien-Gesellschaft, which employ creosote oil or naphthalene for extracting the bitumen from pitch; and in the Ger. P. 213507 of the Chemische Fabrik Lindenhof, C. Weyl & Co., where phenols are described as the solvent for this purpose. The phenols are more easily removed from the solution than the above-mentioned solvents, by a treatment with alkalis, and the bitumen prepared in this way, in consequence, has a higher softening point than that which is obtained by extracting the pitch with hydrocarbons.

The Distillation of Pitch for Coke.

Long before the technical importance of anthracene had been recognized, attempts were made to obtain further products from the pitch left behind after the distillation of coal-tar. The reason for this was the fact that coal-tar pitch was not at that time consumed in any large quantity, except for patent fuel, and that with only this single opening the article would be very liable to become unsaleable. The idea of carrying on the distillation till all the volatile products are given off and only coke remains (for which there was always a certain sale) was very plausible. The motive for doing so became much stronger as soon as the discovery of artificial alizarin had raised anthracene to the rank of the most valuable component of coal-tar. It was known that the pitch contains some anthracene; and the hope of obtaining it therefrom at a profit seemed justified.

The apparently simplest plan, that of carrying on the process in the tar-still itself to the stage of coke, is not feasible. We have seen, on p. 397, that cast-iron is not well adapted for tar-distilling, and wrought-iron would be burnt away too quickly. Moreover, cutting out the coke would be very costly, and would seriously injure the iron plates. A method proposed by Puls (B. P. 1910, of 1858), viz., adding earthy substances to the tar, so as to prevent the red-hot residue from adhering to the still, would cause the loss of the coke, and is not worthy of serious consideration.

Hence distilling the tar up to pitch in the ordinary stills, and distilling the pitch in separate vessels, either charging them with it in the solid state, or running it while still liquid into the pitch-oven, cannot be avoided. The oven may be a brickwork muffle, or a fireclay gas-retort, or an iron vessel of some shape or other.

The brick pitch-ovens, which were formerly sometimes employed,[1] will be but briefly mentioned here, as they have not proved practically successful. They were muffle-furnaces, about 15 ft. long, 6 ft. wide, and 6 ft. high to the crown of the arch, fired by zigzag flues running underneath the concave-shaped furnace-bed. At each gable-end there was a working-hole, about half-way up, closed during the process. The vapours were carried away by a cast-iron pipe, 90 ft. long, and were condensed by air-cooling. Usually two ovens were built side by side, each was charged with 2 tons of pitch, the doors closed with metal plates fastened like gas-retort covers and screwed down. The fire having previously been lighted, volatile products were soon formed, which were condensed in the cooling-pipe and collected in a tank. The oil first coming over resembled the last distillates from coal-tar; the following portions were more viscid, very dark, and empyreumatic. After about twelve hours, when the distillation was nearly finished, large quantities of heavy yellow vapours appeared, condensing partly to a very thick pasty mass; sometimes they yielded a reddish-yellow pulverulent substance, which on exposure to the air soon turned soft and sticky, and contained much pyrene, chrysene, and other hydrocarbons. When nothing more came over, the two gable-end doors were cautiously opened; the vapours inside the muffle took fire, and the soot adhering to the sides and the arch was burnt. The dense smoke then issuing from the doors was aspirated by a vapour-hood and conveyed to a chimney. The cold current of air caused the layer of coke on the furnace-bed to crack and break up into pieces, the attendant using iron tools to accelerate the process. The coke was drawn out red-hot and quenched with water. It was quite honeycombed, owing to the escape of vapours from the pasty mass. The heat produced by the burning of the soot kept the oven red-hot, so that very little fuel was required for the next operation. One hundred parts of pitch yielded 25 parts of oil, which could be mixed with the creosote oil or sold as a common lubricant, and 50 parts of coke; 25 parts were lost. But these were *maximum* yields; in practice very much pitch was lost by leaking through the brickwork, and hence the yield was smaller than from the iron retorts.

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[1] Figured and described in Ronald and Richardson's *Chemical Technology*, i., p. 541.

Of later statements upon this subject, dating after the invention of alizarin, we shall first quote a report made by Behrens,[1] upon experiments made by him on a large scale. He employed a cast-iron retort in the shape of a horizontal box 13 ft. long, 3 ft. 8 in. wide, and 3 ft. 8 in. high, constructed of 16 flanged plates, bolted together and joined by rust cement. The front and back openings were closed by iron doors and luted with lime-putty. On the top of the retort there was a manhole for charging with solid pitch, and a cock for charging with liquid pitch, and also a safety-valve and a 6-in. pipe for the vapours. The latter was connected with an iron box provided below with a swan-neck pipe to run off any liquid, and on the top with a pipe for carrying away steam and uncondensed vapours into a condensing-worm. The retort was set on a flat arch, which was levelled above and heated from below by a fireplace in front; at the back the flame divided into two parts, returned through two lower flues on each side of the retort, to the front, and once more, through two upper flues, to the back. At first a little water comes over, especially with damp pitch, and hence cautious firing is necessary to prevent boiling over. But as soon as the pitch is fairly boiling, oily matters condense, and the distillation goes on rapidly even with moderate firing, so that 3 tons of pitch can be distilled in three or four hours and yield 14 or 15 cwts. of oils. The latter are condensed in two fractions—the first as anthracene oil, the second as lubricating oils. From the beginning, with these arrive water, gases (especially ammonia[2] and hydrogen), benzene, naphthalene, and volatile oils (of sp. gr. 0·97). When two-thirds of the oil have distilled, the formation of coke commences; the mass swells; and if the retort has been fully charged, the fire must now be slackened.

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[1] *Dingl. polyt. J.*, ccviii., p. 371.

[2] Watson Smith also has observed the evolution of ammonia in the coking of pitch (*J. Chem. Soc.*, 1884, pp. 144-8).

When the production of oil is nearly finished, the more volatile hydrocarbons decrease, but there is even more steam and gases. At last there appears a reddish-yellow resinous sublimate, which gradually ceases, and the evolution of gases ceases also. The retort is now carefully opened, and the gas issuing from it is lighted; otherwise the access of air might cause an explosion. There were obtained:—

Oils containing anthracene . . .	27 to 30 per cent.
" " chrysene and pyrene . .	
Sublimed reddish-yellow resin . .	
Coke	48 " 52 " "
Gases, steam, and 0·2 per cent. light oils .	25 " 28 " "

The crude anthracene oil, on treatment with alkalis, yielded 3 per cent. of an oil soluble in alkalis, and separable again by sulphuric acid, which on distillation gave 8 per cent. of water, then increasingly viscid oils, and, above 360°, a transparent wine-coloured solid mass; a little carbon remained behind.

The following apparatus of Fenner and Versmann for coking pitch has been worked on a large scale. The tar is first distilled in an ordinary wrought-iron still; that shown here (A, Fig. 134) is shaped like a horizontal boiler. B is the condenser for light oils and creosote oil. When the anthracene oil is about to come over, the liquid pitch is run, while still hot, into a series of cast-iron vessels C C C, in which the coking is effected. It passes through the tap *c*, the main pipe D, and the taps *d d d*, into each of the pitch-stills. Figs. 135 and 136 give details of the latter. They are made of cast-iron, and are about 4 ft. in diameter, and 4 ft. 8 in. deep (inside measurement); it is alleged that, when set in the way indicated in the diagram, they will last five or six years, distilling off one charge of 1½ to 2 tons of pitch every three days—one day being occupied in the distillation, and two more in the cooling, emptying, and recharging. A production of 10 tons of pitch per day therefore requires three sets of six cast-iron pots each for the coking-operations. *a* is the cast-iron pitch-still; *b*, furnace; *c c c c*, flues; *d*, pitch-delivery pipe; d^1, stopcock; *e*, condensing-tube for the vapours evolved; e^1 e^1 e^1, branch pipes delivering condensed liquors to the tank; *f*, condensing-chamber; *g*, tank.

The vapours evolved are condensed entirely by atmospheric cooling, partly in the tube *e*, partly in the condensing-chamber The evolution of vapours is greatly facilitated by creating a partial vacuum in the still *a* by means of an exhauster or blower attached to the exit-pipe of the chamber *f*; but no advantage is gained by blowing either hot air or steam through the pitch (*cf.* p. 455). Towards the latter part of the distillation

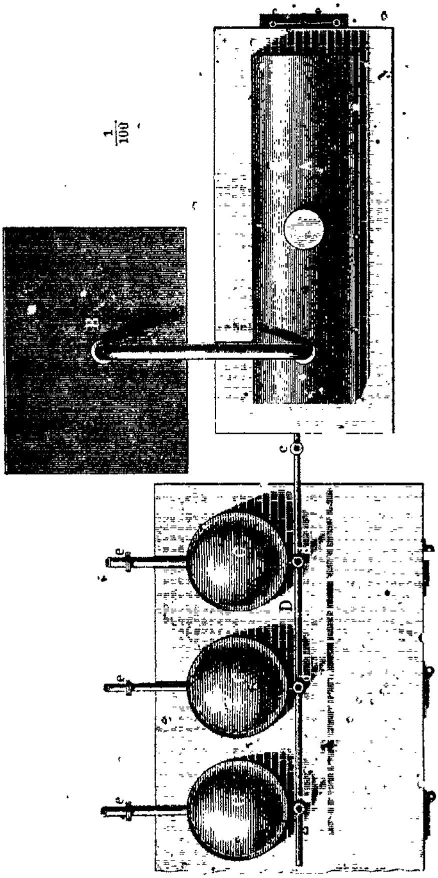

FIG. 134.

the branch tubes e^1 e^2 e^3 are successively opened, so as to provide as short and ready a passage as possible for the escape

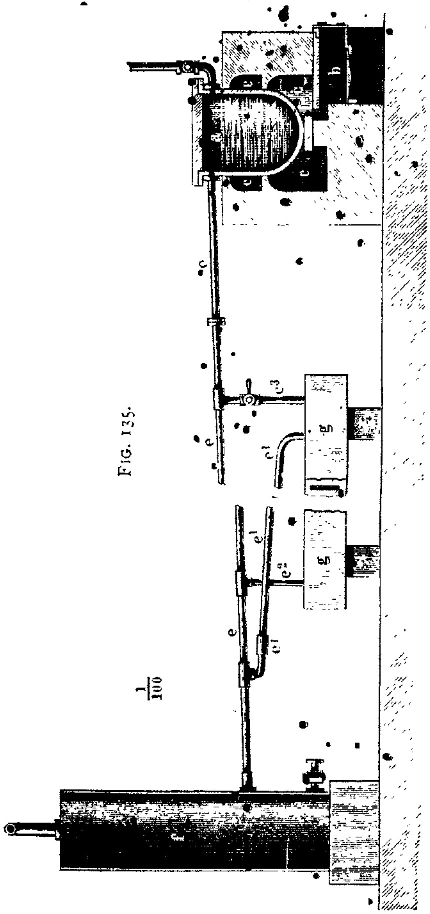

FIG. 135.

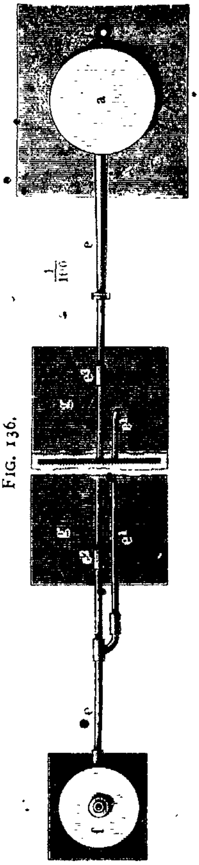

FIG. 136.

of the condensed substances into the tank *g*. This is essential; otherwise the vapour-delivery pipe *e* is apt to become blocked up by the separation of solid matter.

The distillate of 315° to 370° C. according to Fenner and

Versmann is very rich in anthracene, but little naphthalene or chrysene is present; between 260° and 315° the naphthalene is in excess; above 370° anthracene is less abundant, chrysene and other bodies of higher boiling-point than anthracene being the main constituents of the distillate. On standing, these distillates deposit solid matter, from which crude anthracene is separated by filtration, washing with lighter oils, and pressing, as will be described in the next chapter.

This plant may also be used for the distillation of pitch purchased in that state for the extraction of *anthracene* from it. For this purpose the pitch is broken up into small lumps and, preferably, mixed with oils obtained in a previous distillation, or with dry absorbent carbonaceous matter. The object of this is to prevent frothing and the blocking-up of the vapour-delivery tubes on first heating, owing to the presence of moisture in the pitch. The patentees state that, on an average, 2 per cent. of anthracene is thus obtainable from ordinary pitch. As ordinary coal-tar yields about 0·5 per cent. of crude anthracene and 67 per cent. of pitch (this latter corresponding to 1·33 anthracene per 100 of original tar), it follows, according to the patentees, that the production of anthracene is nearly quadrupled when the tar is coked—*i.e.*, all together, 1·85 per cent. is obtained instead of 0·5 per cent., if the above statement be correct. Unfortunately "pitch-anthracene" has been found to be so much contaminated with chrysene, etc., that the alizarin-manufacturers cannot very well purify it, and will not work with it at any price. Several lawsuits have arisen from this circumstance, and the manufacture of pitch-anthracene seems to have been entirely abandoned. It could hardly be otherwise, as the production of ordinary anthracene in the United Kingdom alone was in excess of the demand of the whole world (see next chapter). The coke left behind is very good (see below); and the oil from which the anthracene is separated is an efficient lubricator; this is actually the only opening for the pitch-oils in general, until some better method of purifying the pitch-anthracene be discovered.

The statements of Fenner and Versmann concerning the amount of anthracene obtainable from pitch seem to be strongly exaggerated. Watson Smith (priv. comm.) obtained from ordinary hard pitch by distilling, mixing the distillate with mother oils; and redistilling, no more than 0·556 per cent. crude anthracene from the pitch, or 0·33 from the tar.

The proposal of E. Kopp (p. 453) might be referred to this chapter also.

It is asserted that since the introduction of steam in the last stage of tar-distilling all the anthracene is taken out of the pitch, and that it is thus from the outset impossible to work the pitch for anthracene, as there is none in it.

One of the principal difficulties in the distillation of coal-tar pitch, which prevents this operation from being very extensively employed, is that of finding a suitable material for the retorts. Brick muffle-furnaces leak too much; fireclay retorts require too much fuel in proportion to the quantity of pitch worked up; cast-iron is quickly destroyed by the heat and the pitch, although Fenner and Versmann assert the contrary respecting their construction figured above.

F. von Dahmen and P. Hagyi Ristic & Co. obtained a German patent (No. 166972) for making coke from tar or pitch, by running them in a boiling-hot state into white-hot retorts, by which process a very dense coke is obtained (*cf.* p. 373).

Kridlo (Aust. P. appl. K.32742, of 1908) seeks to evade the difficulty of finding a suitable material for pitch-distilling retorts, by simply utilizing the heating-power of the pitch, and abandoning the volatile products. He throws the pitch on to a grating, fixed over a fireplace serving for some other purpose; here the pitch melts and runs down in thin streams, which give off most of the volatile substances, so that it arrives below as solid coke, consisting of nearly pure carbon.

Watson Smith (*J. Soc. Chem. Ind.*, 1892, p. 119) noticed a distinct smell of *ammonia* when coking tar-pitch, but only on cooling, also in dry air long after the hydrocarbons have passed over. Alder Wright noticed besides this a smell of *cyanogen*.

Quality of Pitch-coke.

The *coke* obtained by distilling pitch is very good if properly made, but only in that case. This subject has been treated in detail by Behrens (*loc. cit.*). The quality of the coke depends upon the temperature at which it has been made, and upon the length of time during which it has been exposed to that temperature. If both are insufficient, a dull, blackish, compact mass is obtained, with but few cracks. On opening the retort this coke takes fire and burns with a luminous flame issuing through the cracks of the mass. Although the coking is somewhat promoted by such burning-out, and the cracks are widened with a crowbar, the quality of the product is very inferior, owing to all pitch-coke, except the very hard-burnt kind, crumbling to dust in the fire. Hence coke that is only burnt out afterwards possesses but very little cohesion; and, as it strongly adheres to the sides of the retort, much dust is produced in breaking it up and getting it out. Coke not ignited, having been quenched with water, must from time to time be drenched with water again, as otherwise it easily takes fire. In order to make *hard* coke, the temperature inside the retort, when the red vapours indicating the end of the distillation have disappeared, must be raised to a bright red heat; and this should be kept up for eight hours at least. Thus a complete operation lasts about twenty-four hours. Hard-burnt coke adheres but little to the sides of the retort, possesses great cohesion, and consists of prismatic columnar pieces, which can be got out of the retort almost without using a crowbar. After being once quenched it does not take fire again. It is light grey, very dense, and does not crumble in the fire. Behrens made some experiments with such coke in English iron-works, with the following results. No success was attained in employing it for melting cast-iron in cupolas in lieu of charcoal, or for refining wrought-iron on hearths; in the latter case the slag was not easily separated from the iron. But hard pitch-coke is very good for refining pig-iron in the English way, which is usually done by gas-coke; the refined pig afterwards yielded very good wrought-iron on puddling. This coke is also very well adapted for fusion processes in crucibles.

According to Staveley,[1] pitch-coke contains only 0·11 to 0·12 per cent. sulphur and 2·43 to 2·50 per cent. ashes; it does not crumble even when exposed for months in the open air, as there is no sulphide of iron in it; and it surpasses even the best Durham coke in hardness, density, heating-power, and strength to sustain heavy loads.

Pitch-coke has proved to be an excellent material for the preparation of *electric carbons*.

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[1] *Chem. News*, xlii., p. 228.

Other Uses of Coal-tar Pitch.

Coal-tar pitch is an excellent *reducing-agent* (*e.g.*, for black-ash mixing, for making barium sulphide, etc.), because it is nearly free from ashes and sulphur; but it is mostly too expensive for this purpose, whilst it more frequently pays in the manufacture of ultramarine.

As a factor in the manufacture of *cement-steel* (blister-steel) it has been patented by E. J. Payne and W. Clarke (B. P., 5th Oct. 1872).

It is contended that the iron combines more quickly with the carbon from pitch than with that from any other source.

An attempt made by Behrens (*loc. cit.*) to employ the pitch in *gas-making*, by melting it and running it through a bright-red iron tube, yielded, on an average, for 1 kg. pitch, 250 litres of gas, but almost devoid of illuminating-power. It consists mainly of hydrogen, and contains some sulphur, and would therefore be hardly of any value in gas-making.

Balfour and Lane (B. P. 12721, 1886) add from 5 to 10 per cent. of soft pitch to the coal used in the manufacture of illuminating-gas, in order to get more and better gas, richer in benzene, and denser coke, containing little sulphur. The improvement in the quality of gas would seem to be very doubtful.

Kraemer proposed to utilize any excess of pitch by adding it in small portions to coal, coked in ordinary coke-ovens. This yields pure coke of excellent quality.

Kent (Ger. P. 194372) prepares *lubricating* oil, free from phenols and naphthalene, by distilling pitch from water-gas tar and gas oils.

The method of Markl, mentioned on p. 498 (for which, besides the Ger. P. 277502, he obtained the B. P. 10383, 1914), is applicable also for treating pitch.

Douglas Bros. (Ger. P. 125455) manufacture *acid-* and *steam-*proof vessels by lining them with bricks, formed of coke, soot, retort-carbon or graphite, cemented together by pitch or tar and ignited; the mortar for keeping those bricks together consisting of the same substances.

When pitch cannot be utilized in any other way, it can be *burned to lampblack.* The furnaces and condensing-chambers for this purpose are similar to those described on pp. 252 *et seq.*

for burning tar; only, as the pitch is solid, it must from time to time be thrown upon the red-hot iron plates on which it is to be burnt. No doubt a vessel might be fixed above these, where the pitch would be melted by the combustion going on below, and from which it would be run out continuously by means of a valve in the bottom. According to Thenius 500 kg. of pitch yield 200 kg. of different descriptions of lampblack, and 200 kg. of coked residue, which is knocked off with hammer and crowbar and used as fuel. Along with pitch any dry alkaline residues from purifying the tar-oils may be burned; but usually none are obtained, as the alkali is employed in aqueous solution.

Disease caused by Pitch (Pitch Cancer).[1]

The men who have to handle coal-tar pitch are sometimes afflicted by a peculiar skin disease known by the name of "pitch-cancer," and specially investigated by Ehmann (*Z. J. Gew.-Hyg.*, 1909, p. 574; *Chem. Zeit.*, 1910, p. 17). Its symptoms are a brown coloration of the skin ("Indian" skin), eruption of grubs or maggots on the skin, yellow coloration of the conjunctiva. This disease occurs principally at patent-fuel works, but also in other industrial establishments where coal-tar pitch is manipulated. A detailed report on it has been made by the English factory inspector, Dr Legge (*Chem. Trade J.*, 1910, xlvi., p. 506). He describes manifold forms of it, both acute and chronic, and recommends cleanliness as the best preventative against it. The rules laid down by him are as follows (abstract):—

Duties of the Employers.—1. There shall be provided and maintained in a cleanly state and in good repair (*a*) Suitable bath accommodation (douche or other) in the proportion of at least one bath for every five persons employed on a shift, with hot and cold water, soap, and towels; (*b*) A lavatory with a sufficient supply of clean towels, soap, and nail brushes; (*c*) Overall suits, closely fitting at the neck, wrists, and below the knee, for all persons employed, to be washed or renewed at least once every week; (*d*) Suitable places for the deposit of clothing taken off during working hours. 2. All disintegrating machines and elevators to be encased except at the point where charging is done. 3. Wire goggles, or other equivalent for the eyes, to be provided for the persons employed in unloading, digging, breaking, or crushing the pitch.

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[1] Cf. *supra*, p. 314.

Duties of Employees.—A bath to be taken at the works at least once every alternate week-day, except in the case of workmen who can produce a medical certificate that such bathing would involve risk in his then state of health. Every person employed shall wash before leaving the works for meals, or at the end of the day, when a bath is not taken; and shall wear the overall suits provided as above, and the goggles for protecting the eyes.

H. W. Robinson (B. P. 4159, of 1913; U.S. P. 1114045) removes from tar and pitch the property inducing pitch-cancer, by adding formyl aldehyde or other aldehydes to the tar or pitch during the distillation, preferably after the separation of the carbolic acid fraction and before the separation of the heavy oil fraction, and a further quantity of the aldehyde may be added to the pitch residue after the completion of the distillation. The aldehyde is preferably introduced into the still in a steam jet, for which purpose an apparatus is described.

Testing of Pitch.

The testing of pitch is principally performed with regard to its application for the manufacture of patent fuel (briquettes) and asphalt, and ordinarily comprises the estimation of its specific gravity, of free carbon, of mineral impurities, of the temperature of softening and fusing, and of the coking-residue.

Sometimes it is the question of identifying coal-tar pitch as such, or proving its presence in other descriptions of pitch or natural asphalt.

The estimation of specific gravity is performed by the usual methods, bearing in mind that the pitch (especially hard pitch) frequently contains cavities filled with air, and that, therefore, it should be reduced to powder before estimating its specific gravity. The ordinary specific gravities are (roundly):

Of soft pitch	1·250 to 1·265.
„ middling soft pitch	1·275 „ 1·280.
„ hard pitch	1·285 „ 1·330.

Free carbon is estimated by the methods described *supra*, pp. 308 and 523. The method usually employed is that prescribed by Kraemer and Spilker, viz., extraction with aniline and pyridine bases (*supra*, p. 524). Constam and Rougeot (*loc. cit.*) perform the extraction by benzol or carbon disulphide, but Russig (*Chem. Zeit.*, iv., No. 19) objects to this, both on account of being unreliable and requiring far too much time (up to four or five days!). This also holds good of the method of Hodurek, described *supra*, p. 524. The only method to be recommended, besides that of Kraemer and Spilker, is that of the Chemische Fabrik Lindenhof, C. Weyl & Co. (Ger. P. 213507), employing phenol as a solvent.

Coking-residue.—This test, according to Muck (*Z. f. Berg, Hutten und Salinenwesen*, vol. xxxvii.), is very important for judging of the quality of the pitch; not the quantity, but the physical appearance of the coke, whether it be porous or sintered, since this indicates the behaviour of the briquettes when used in firing. Such descriptions of pitch which furnish a thin liquid on fusing allow the gases and vapours formed to escape without leaving a porous coke behind. But pitch which leaves a swelled-up, porous coking-residue (which frequently occurs in the case of hard pitch containing a large proportion of free carbon, but also in the case of soft blast-furnace pitch, such as is formed from the substances contained in the deposits of blast-furnace outlet-gases) is not fit for the manufacture of briquettes.

According to Brookmann (quoted by Constam and Rougeot in *Z. angew. Chem.*, 1904, p. 845) Muck's coking-test is carried out in the pit laboratory at Essen in the following way:—One g of the finely powdered pitch is heated in a platinum crucible, the cover of which has in the centre a hole of a diameter of 2 mm. The heating takes place in the hottest part of the flame of a Bunsen burner, the bottom of the crucible being about 6 cm. above the mouth of the burner, and is continued until no more jets of flame appear above the hole in the cover of the crucible. To make sure of it, when there is no flame coming out of this hole, another flame is brought in contact with it. The appearance of the coke formed is observed before going on to the estimation of the *ashes*, which is performed with the coking-sample in the usual manner.

Estimation of the softening- or melting-point.—This is the most important test for the quality of the pitch intended to be used in the manufacture of briquettes.

Soft pitch (*brai gras*) softens at 40°, melts at 60°.
Moderately hard pitch „ 60°, „ 100°.
Hard pitch (*brai sec*) „ 100°, „ 150° to 200°.

A practical test is kneading a sample between the teeth. If this can be done easily, the pitch is soft; if with more difficulty, it is moderately hard; and if it is crushed to powder, it is hard. Soft pitch is more shining and black than very hard pitch, which verges upon grey and has less lustre. Sometimes the latter is even a little porous: if it is more so, it is partly coked and cannot be used for patent fuel. The specific gravity of hard pitch is about 1·3.

A test for soft pitch, to see whether it is suitable for patent fuel, is dipping a piece of about 4 in. length and ¾ in. diameter for two minutes in water of 60°; when taken out it should bend without breaking. For harder descriptions water of 70° is taken; on the other hand, it is sometimes required that pitch should easily twist at 55°.

I am indebted to Mr F. G. Holmes, of Messrs Burt, Boulton, & Haywood, for the following notes on a method for testing pitch (softening- and fusing-point):—

"Several pieces of pitch are taken from different parts of the sample and cut to the size of a ½-in. cube. These cubes are then fixed on metal wires by heating the ends of the wires and pressing them into the pieces of pitch, which are then suspended in a vessel containing about 500 c.c. of water heated by any convenient means, at a uniform rate of 5° C. per minute, as indicated by a thermometer immersed in the water with the bulb about 1½ to 2 in. from the bottom of the vessel.

"The cubes are suspended on a level with the bulb of the thermometer. As the temperature rises, the pieces of pitch are taken out from time to time and twisted or squeezed with the fingers, and the temperature noted at which they assume the following conditions:—

(1) Readily twisting or soft.
(2) Very soft.
(3) Fused.

(1) The twisting-point is when the pitch can be easily twisted round several times.
(2) Very soft, when it yields to a very light pressure of the fingers.
(3) Fusion, when the pitch melts off the wire."

More accurate results are obtained by the following contrivance (originated in France, and also communicated by Mr Holmes). The tin cylinder, Fig. 137, contains a horizontal partition, in which five tubes are inserted, closed at the bottom. The central tube serves for introducing a thermometer, the other four tubes are filled with ground-up and sifted pitch. The sifting must remove both the coarse particles and the dust. The pitch-powder is weighted by an iron disk attached to a pin of definite weight, the perforations in the top cover serving as guides for the pins and the thermometer. The cylinder is now filled with water a little above the tops of the tubes, and is heated over a lamp till the disks sink down into the melted pitch, the temperature being noted at that point.

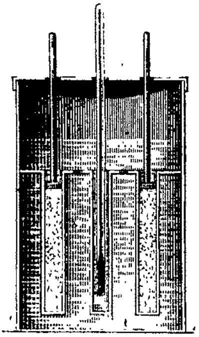
FIG. 137.

Muck[1] moulds the samples into cylindrical sticks, 4 mm. thick and 100 mm. long, which are bent round for a length of 20 mm., so that the shorter limb can be attached by an india-rubber ring to the mercury vessel of a thermometer, whilst the longer limb is parallel with the stem. The whole is immersed in a beaker provided with a mechanical stirrer and filled with water, and this is cautiously heated until the longer limb begins to turn down.

Buchanan[2] sticks a piece of pitch to a thermometer, placed in a dry test-tube and heated in a water-bath. The pitch first softens and then falls off. This happens with hard pitch at 80°, with medium hard at 55°, and with soft pitch at 50° C.

Schenk zu Schweinsberg[3] prepares, from a glass tube 7 mm.

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[1] *Zsch. f. Berg-, Hutten- u. Salinenwesen*, 1889

[2] *J. Soc. Chem. Ind.*, 1894, p. 1098.

[3] *Z. angew. Chem.*, 1890, p. 704.

wide and 25 cm. long, the apparatus shown in Fig. 138. The lower portion up to *e f* is filled with ground pitch *p*; if too soft for grinding, the pitch is moulded into small pellets. A drop of mercury is poured in, and the narrow part of the tube is drawn out into a capillary (as shown in the right-hand side). A platinum wire, *a*, *b*, *c*, *d*, *q*, is attached to it as shown in the figure, the loop at *d* serving for putting in a glass rod, by means of which the whole is suspended in a beaker filled with water, together with a thermometer whose bulb is at the same level as the pitch. The water is very slowly heated, and any gas-bubbles are removed from the glass tube by means of a feather-quill. As the heat increases, the pitch sinters down to about half its original volume. When its fusing-point is reached, this is shown by a swelling up. The commencement of the fusion is most easily seen in the lower bend and at the point of the tube. The thermometer is now read, to establish the fusing-point, but the heating is continued until the pitch rises in the tube and the drop of mercury sinks down and is enclosed by the liquid pitch, so that the whole of the lower part of the tube is filled with liquid pitch and mercury. This point, at which the temperature is again noticed, is called the "practical" fusing-point; it is below 50° C. for soft pitch, 60° to 99° for medium-hard, and above 100° for hard pitch.

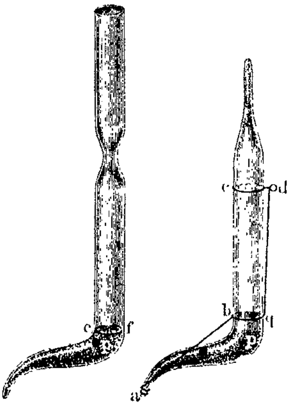

FIG. 138.

Klimont[1] approves of this test, but only when carried out by a person who has much experience with it. He prefers employing an ordinary test-tube, the bottom of which is charged with powdered pitch and which is suspended in a beaker alongside a thermometer. For hard pitch the beaker is filled with glycerine, for soft pitch with water, and it is very gradually heated until the surface is smooth and shining. This is the melting-point. He also describes another method, which must be consulted in the original.

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[1] *Z. angew. Chem.*, 1900, p 761.

Mabery and Sieplein[1] employ a glycerin bath (Fig. 139), in which is placed a narrow beaker B closed by a cork, through which passes the thermometer C and a metal strip D, ½ in. broad, ending ½ in. above the bottom of B, where it is bent upwards. On this is placed the sample of asphalt or pitch E. This sample must form a slab, 1 in. long, ½ in. wide, ⅛ in. thick, so that it projects over the strip D. The thermometer should be ⅛ in. distant from the sample. The heating is continued up to the point where the sample has sufficiently softened to bend down on both sides of the metal support.

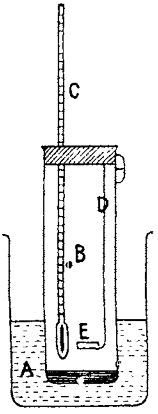

FIG. 139.

Kraemer and Sarnow[2] declare the following method for estimating the softening- or melting-point to be most reliable. Melt about 25 g. pitch in a small tin vessel with level bottom in an oil-bath of similar shape at about 150° C., so that it forms a layer 10 mm. deep. Into this dip one end of a glass tube, open at both ends, 6 or 7 mm. wide and 10 cm. long. Close the upper end of this with the finger, take it out of the glass and allow the pitch contained in the other end to cool in a horizontal position, turning it round all the time. When the pitch is no more liquid, it will occupy a height of about 5 mm. Remove the pitch adhering outside, and pour upon the pitch in the tube exactly 5 g. mercury, measured off in a small tube provided with a mark. Suspend the tube (or a number of them) in a small beaker, filled with water, place this in a larger beaker filled with water, put a thermometer in a smaller beaker in such manner that its mercury vessel is on the same level as the pitch sample, and heat with a small flame. The temperature at which the mercury breaks through the pitch is noted as the fusing- or softening-point. For samples of a fusing-point above 90° C., the outer beaker is filled with white paraffin oil, the inner one with saturated solution of common salt or magnesium chloride. The results obtained are rather lower than by the old capillary method, but are quite constant and therefore well adapted for comparison.

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[1] *J. Amer. Chem. Soc.*, 1901, xx., p. 16; *Chem. Centr.*, 1901, i., p. 809.

[2] *Chem. Ind.*, 1903, p. 55.

E. A. Kolbe ("Inaugural Dissertation," Zürich, 1908) ascertained the melting-points of ten samples of French coal-tar pitches (sp. gr. 1·252 to 1·271) by Kraemer and Sarnow's method, as described in the text, and found them to range between 105° and 129° C. Other communications on Kraemer and Sarnow's method have been made by Margosches (*Chem. Rev. Fett-Ind.*, 1904, part 12) and Wendriner (*Z. angew. Chem.*, 1905, p. 622).

Other apparatus for determining the fusing-point of pitch have been described by Kovács (*J. Soc. Chem. Ind.*, 1902, p. 1077); Church (*J. Ind. Eng. Chem.*, 1911, p. 230); Bauer (*Chem. Centr.*, 1905, ii., p. 1745).

Wendriner (*Z. angew. Chem.*, 1905, p. 1946) shows that a very slight percentage of water in pitch causes great irregularities in the fusing-points. Russig (*Chem. Zsch.*, iv., 464, 543; v., 363) considers differences of 2° or 3° in the fusing-points of pitch to be of no moment whatever, since the fusing-point, hardness, and cementing power do not run parallel in pitches of different origin.

Köhler cites the following specification for pitch intended for the manufacture of briquettes:—(1) Pieces of $\frac{3}{16}$-in. thickness are placed in water of 60° C.; after this has cooled down to 55° the pitch may be easily twisted without breaking. (2) When carbonized in a crucible before a gas-blast at a bright red heat, it should not leave more than 45 per cent. residue. (3) It should be pure coal-tar pitch, softened with anthracene oil, not with creosote oil or naphthalene (which could be proved by distillation), in which case it fouls the pistons of the presses.

Testing the Consistency of Bituminous Binders in the Asphalt Paving Industry.—An apparatus for this purpose has been constructed by C. N. Forrest, and is made by Howard & Morse, Brooklyn, N.Y. It consists of an aluminium saucer and a conical brass collar, which is filled with the bitumen under examination. The whole is immersed in water of 90° F., and the number of seconds is noted which elapses until the mass has been forced out of the collar and the apparatus sinks below the surface.

The *viscosity* of pitch-like substances is tested by Trouton and Andrews[1] by means of torsion. A constant torque is applied to a cylindrical bar of the material, and the relative motions of the ends are observed, from which and from the dimensions of the cylinder the viscosity is calculated.

Binder[2] prefers testing the pitch for briquettes by making small briquettes of about an inch diameter with various mixtures, and testing these by means of a specially constructed press, heated by gas. Later on[3] he describes his apparatus more fully. He uses a small cylindrical steel mortar, as employed in the analysis of minerals, heats it to 100° to 150° C., puts the mixture of pitch and sand or coke-powder into it, and compresses it by putting on the pistil and giving three or four heavy blows with a hammer.

Estimation of the Bituminous Substances in Pitch.—For more exact tests the real "bitumen," as distinct from "free carbon" (coke) and ashes, is quantitatively estimated. This can be done in the way usual for testing bituminous coal for the yield of coke, viz., by heating say 1 g. of finely powdered pitch in a platinum crucible of 1¼ to 1½ in. height, with the lid on, by means of a good Bunsen burner, first gently, till no more smoke and flames issue between the crucible and its lid, then as strongly as the burner will permit. The operation should last about twenty minutes. The crucible is placed in a desiccator and the coke is weighed after cooling; it amounts to from 25 to 50 per cent. of the pitch.

For a direct estimation of the bituminous substances as distinct from "free carbon," in pitch, it is successively treated with hot benzene, carbon disulphide, and alcohol, and this treatment is again repeated. The operation is conveniently carried out by means of a Soxhlet's extracting-apparatus. Since the fine dust easily passes through a filter, it is sometimes preferable to simply boil the pitch in a flask with reflux-cooler and to decant through a filter. The residue left may be considered as "free carbon" (more properly speaking, coke). We refer to the details of this process in Chapter V., p. 523.

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[1] *J. Soc. Chem. Ind.*, 1904, p. 680.

[2] *Chem. Zeit. Rep.*, 1899, p. 194.

[3] *Z. angew. Chem.*, 1905, p. 954.

Constam and Rougeot[1] estimate in briquette pitch both the coke residue obtained by heating, as above, and by extracting the pitch with disulphide of carbon. Russig (*Chem. Zeit.*, iv., No. 19) does not approve of this solvent being used by itself, the results being uncertain, since the percentage of substances soluble in carbon disulphide in coal-tar pitch varies within wide limits (from 60 to 95 per cent.).

Kraemer and Spilker[2] consider the percentage of bitumen in pitch as the most important test for its briquette-making quality.

Russig (*loc. cit.*) also believes that the estimation of the real bitumen in pitch is the proper test for its suitability for the manufacture of briquettes, but he does not consider the methods for this purpose to be sufficiently developed. More particularly he does not think the fusing-point of pitch as a sufficient criterion of its quality (to which opinion Wendriner, in *Chem. Zeit.*, 1905, p. 543, makes some objections).

Hodurek (*cf. supra*, p. 524) exhausts the pitch with boiling benzol, thus obtaining a precipitation of "suspended carbon and bitumen." The "suspended carbon" by itself is found by dissolving the pitch in anthracene oil, filtering, and only then precipitating with benzol, the "bitumen" being found by difference against the first test.

J. E. Mills (*J. Soc. Chem. Ind.*, 1908, p. 887) quotes the following tests, employed at the U.S. Government fuel-testing works at St Louis, for the testing of briquette pitch. The material is distilled; all coming over below 270° C. is rejected as valueless. The flowing-point should not be below 70°. The smaller the residue remaining on extracting the pitch with carbon disulphide, the more suitable the material is for briquetting. The higher the flowing-point, the better the briquettes stand in the fire; if it is so high that the working of the machines becomes difficult, it is lowered by the addition of heavy tar-oils boiling under 270° C.

Leo (*Chem. Zeit.*, 1909, p. 359) has worked out a colorimetric method for use in patent-fuel works which permits of judging of the quality of the pitch in a quick and easy manner. It is founded on the brown colour, imparted to benzol by pitch, which is all the more pronounced, the greater the proportion of pitch. Samples are taken at certain intervals, of the coal and the pitch before mixing them, and of the briquette mixture after coming out of the heating-furnace. The samples are reduced to an average sample of from 1 to 0·5 kg. and dried at 100°, to estimate the moisture. Of these ground and well-mixed samples about 50 g. are weighed out, which are fused in an oil-bath at 150°, and after cooling ground to a fine powder. From this is prepared, A, a five per cent. pitch solution, by mixing 0·05 g. pitch with 0·95 coal powder, which is placed in a half-litre flask, together with 200 c.c. of colourless commercial 90 per cent. benzol. B, 1 g. of the powdered briquette sample is treated in the same way. Both A and B are heated exactly half an hour, the flasks being closed by a reflux-cooler, cooled, filtered through a double filtering paper into dry flasks, and the filtrates put into Eggertz tubes, holding 20 c.c. and provided with a $\frac{1}{10}$ division. Of the pitch solution A 20 c.c. are put in a tube which is then closed by a glass stopper, and 10 c.c. of the briquette solution B in another tube. If the solution B is darker than A, colourless benzol is added, until the colour of B is the same as that of A. Suppose this were the case, after 4 c.c. of benzol had been added, we should read off 14 c.c.; the solution B therefore contains $\frac{4}{10}$ of pitch more than A; hence the briquette sample contains $\frac{14}{2} = 7$ per cent. of pitch.

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[1] *Z. angew. Chem.*, 1904, p. 845 ; more fully described in Rougeot's thesis, Zurich, 1905.

[2] *Muspratt-Bunte's Techn. Chemie*, 1905, viii., 13.

Further Tests of Pitch.—Church (*loc. cit.*, p 581) determines the *breaking point* of pitch by covering a flat copper dish with a ¾-in. layer of melted pitch, placing this dish into a dish containing water of a temperature 10° or 12° above the breaking temperature desired, and cooling this in such a way that the temperature falls 1° every minute. From time to time he puts the flat blade of a knife below the layer of pitch, and calls that temperature the "breaking-point" at which, on rapidly raising the knife-blade, the layer of pitch is broken. He further makes an *evaporation test*, by heating 10 g. of the pitch during seven hours in a drying-stove constantly to 160°, and weighing the residue. He also makes a *slide-test* by means of a small tin-plate box, the surface of which consists of undulated plate, the undulation being ¾ in. broad, inclined 30°. In the highest undulation a small cube of pitch is placed and pressed down with the finger. The whole is kept during seven hours in a drying-stove at 40°, and the distance measured which the pitch has moved down on the inclined plane.

Distinction between Coal-tar Pitch and Other Descriptions of Pitch and Asphalt.

The distinction between ordinary coal-tar pitch and blast-furnace pitch, according to Buchanan, *J. Soc. Chem. Ind.*, 1894, p. 1098, can be made by determining the amount of ashes and of free carbon. The former never contains above 0·1, the latter 6·8 to 11·1 per cent. ashes. Pitch containing less than 1 per cent. ashes cannot be blast-furnace pitch. Coal-tar pitch contains rarely less than from 25 to 30 per cent. free carbon; coke-oven pitch usually 5 to 7 per cent., rarely above 10 per cent. No distinction is possible by the crucible test for coke-residues, as they behave similarly in that respect. From hard pitch Buchanan got 38, from medium pitch 30, from soft pitch 26 per cent. coke.

Sometimes coal-tar pitch has to be distinguished from *natural asphalt.* It is generally sufficient to heat the sample in a crucible, when the pungent, acrid vapours from tar-pitch can be easily distinguished from the pleasant, bituminous smell of natural asphalt. The former can also be easily recognised by the green fluorescence exhibited by even dilute solutions in benzol, carbon disulphide, chloroform, petroleum spirit, etc. Malo (*Ann. des Ponts et Chauss.*, 1879, t. ii.) describes the following process, worked out by Durand-Claye. The sample of asphalt is extracted with carbon disulphide, the solution is distilled, and the residue dried at moderate heat until it is hard and brittle on cooling. It is then powdered, and 0·1 g. is put into a test-tube, into which 5 c.c. of strong sulphuric acid is poured. The sample is thus left standing for twenty-four hours, protected from air, and then 10 c.c. of water is cautiously added from a pipette, avoiding strong heating. The whole is poured on to a filter and is washed with 100 c.c. water. In the case of natural bitumen the filtrate is colourless or faintly coloured, in that of coal-tar pitch it is dark brown. By preparing samples with a varying percentage of pitch, the proportions of a mixture of the latter with natural asphalt can be approximately estimated.

Hauenstein[1] heats 1 g. of the material to about 200° C.; after cooling, the substance is powdered and mixed with 5 c.c. absolute alcohol. After a short time the presence of coal-tar pitch is shown by a yellow colour of the alcohol, with strong greenish-blue fluorescence, which becomes more pronounced the greater the percentage of pitch.

Donath and Margosches[2] show the presence of coal-tar pitch in "natural asphalt" by proving the presence of anthracene by Liebermann's reaction, *i.e.*, the red colour (caused by anthraquinone) which is produced by caustic soda solution and zinc dust. The same authors later on[3] admit that some coal-tar pitches give only traces of this reaction, and Berger[4] asserts that it may take place just in the case of pure Trinidad asphalt and pure petroleum goudron!

Köhler[5] discourses at length on the distinction of natural from artificial asphalt. He controverts also the assertion of Malenkovic,[6] who considers petroleum pitch as being nearer to tar pitch than to natural asphalt.

Toth[7] also speaks on the difficulty of proving the presence of artificial beside natural asphalt.

A committee of the International Congress for the Examination of Technical Materials, of which G. Lunge was appointed President, reported to the Congress held at Brussels in 1906 on the above subject. The principal contribution to it was an investigation by Lunge and Krepelka on a number of natural and artificial asphalts. The specific gravities of coal-tar pitches, both soft and hard (1·23 to 1·27), are much above those of natural or petroleum asphalts (0·98 to 1·17). The fusing-points are too irregular to allow of any use for distinguishing both kinds of asphalt. The specific gravities of the solutions in chloroform are distinctly higher for coal-tar pitch than for natural asphalt, and so are the "iodine numbers" in both cases (*Chem. Zeit.*, 1904, xvi., p. 177; *Z. angew. Chem.*, 1904, p. 1116).

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[1] Dietrich, *Die Asphaltstrassen*, p. 41.

[2] *Chem. Ind*, 1904, p. 222; *Chem. Centr.*, 1904, i., 1647.

[3] *Z. angew. Chem.*, 1905, p. 1106.

[4] *Bitumen*, 1905, p. 5.

[4] *Chem. Zeit.*, 1906, p. 36.

[6] *Chem. Centr.*, 1905, i., 1283.

[7] *Chem. Zeit.*, 1905, p. 899; *Chem. Centr.*, 1905, ii., 1054.

A distinction between coal-tar pitch (as well as lignite-pitch and wood-tar pitch, therefore not suitable for distinguishing these pitches from one another) from natural asphalt and "grease-pitch" can be made by Graefe's diazobenzolchloride-reaction (*Chem. Zeit.*, 1906, p. 298). He boils 2 g. of the well-ground pitch for five minutes with 20 c.c. of a seminormal caustic soda solution, and to the cooled filtrate he adds a few drops of a freshly made solution of diazobenzolchloride. Owing to the formation of an azo-dye from the phenols extracted from the tar by the above treatment, a red colour is produced, sometimes even a red precipitate (especially in the case of soft pitch, containing a considerable quantity of oily matter). This reaction is weakest in the case of wood-tar pitch, and it altogether fails in the case of natural asphalt, mostly also with grease-pitch.

Loebell (*Chem. Zeit.*, 1911, p. 408) found that the process as described by Graefe does not in all cases give a sufficiently sharp result, wherefore he modifies it as follows:—Two g. of the bitumen is heated in a porcelain dish on the water-bath, well mixed with the same amount of sand, and, after cooling down, thoroughly agitated with colourless acetone in a wide test-tube. If the solution remains colourless, or takes only a faint yellow colour, there is no suspicion of the presence of phenol-containing substances. If, however, the solution is strongly coloured, it is filtered, the filtrate is evaporated till all the acetone is driven off, and the reddish-brown, oily residue is treated, exactly as prescribed by Graefe, with caustic soda solution and diazobenzolchloride solution. In the case of asphalt mastix, or other easily powdered samples of bitumens, the addition of sand to the original samples may be omitted. It seems probable that it will be possible to extract from asphalts the tarry additions by means of acetone, and to obtain from the quantity, the quality, the specific gravity, and other properties of the solution in acetone sufficient data for judging whether light paraffin oil (sp. gr. 0·880 to 0·900) or other tarry additions of higher consistency are present in notable quantities.

The opposite case, viz., an adulteration of coal-tar pitch by the other descriptions of pitch or asphalt, can hardly come into question, since these are mostly dearer to buy than coal-tar pitch.

Cf. also on the discovery of coal-tar pitch in natural asphalt and in the other description of pitches, Lunge's *Technical Methods of Chemical Analysis,* vol. iii., p. 49 (1914), and H. Köhler's *Chemie und Technologie der natürlichen und künstlichen Asphalte,* 1904, pp. 346 *et seq.*

Statistics on Coal-tar Pitch.

Statistics are only obtainable from Germany. That country formerly produced nothing like the quantity which it consumed for the manufacture of briquettes (*cf.* p. 540), and hence until 1902 had to import a large quantity of pitch, as shown in the following table:—

Year.	Pitch imported.	Pitch exported.	Year.	Pitch imported.	Pitch exported.
	Tons.	Tons.		Tons.	Tons
1894	29,977	7,712	1903	8,603	4,354
1895	39,916	8,937	1904	8,106	4,074
1896	52,088	9,617	1905	6,565	4,119
1897	48,248	7,099	1906	27,057	12,880
1898	52,700	4,888	1907	20,233	16,892
1899	64.692	4,630	1908	39,251	22,389
1900	55,415	4,350	1909	28,434	34.817
1901	59,488	4,613	1910	18,150	52,270
1902	24,266	5,152	1911	40,738	109,700

As pointed out by Russig (*Chem. Zeit.*, 1907, p. 18) these data are incomplete, the importation of coal-tar pitch having been much more considerable than the official figures given above. Up to 1905 coal-tar pitch had been thrown together with other kinds of merchandise.

The strong decline in the importation since 1901 was caused by the development of the recovery of tar in the manufacture of coke (p. 94), and this has led to the consequence that Germany now produces practically all the pitch she requires.